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THE SOLUBILITY OF IODINE IN DILUTE POTASSIUM IODIDE SOLUTIONS.[1]

BY A. A. NOYES AND L. J. SEIDENSTICKER.

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FROM the investigation of Jakowkin[2] on the distribution of iodine between carbon disulphide and tolerably dilute potassium iodide solutions, it would seem almost beyond doubt that the iodine in these solutions is present chiefly in the form of the compound KI_3. This assumption, however, is apparently in contradiction with the well-known fact, which has been quantitatively confirmed by the experiments of Dossios and Weith,[3] that from a strong solution of potassium iodide which has been saturated with iodine, the iodine is, for the most part, precipitated by dilution with water, for the following equation of equilibrium must evidently hold true :

$$KI_3 = k\,(KI) \times (I_2)$$

where the symbols represent the concentrations of the substances, and k is a constant. If now the solutions are kept saturated

1 Read at the Boston meeting of the American Chemical Society, August 25, 1898.

2 *Ztschr. phys. Chem.*, **13**, 539; **20**, 19.

3 *Ztschr. Chem.*, 1869, 379.

with iodine, then its concentration is constant, and the above equation becomes

$$(KI_3) = k\,(KI).$$

That is, the concentration of the periodide is directly proportional to that of the iodide, and dilution should bring about no separation of iodine. It seemed now not improbable that this apparent contradiction between the results of Jakowkin and those of Dossios and Weith could be explained by the fact that the former results have reference to fairly dilute, and the latter to concentrated solutions. The purpose of this investigation was to test this explanation, and at the same time to establish the application of the law of mass action in such a case; namely, a case where a salt solution is saturated with a substance which forms with the salt a simple chemical compound. To this end, we have determined the solubility of iodine in potassium iodide solution between the concentrations of 0.1 and 0.0008 normal, as well as in pure water.

The requisite potassium iodide was obtained by twice recrystallizing a commercial preparation, and the iodine was prepared by sublimation from a mixture of it with potassium iodide. Two solutions of known strength, about 0.1 and 0.0067 normal, were prepared by weighing out the salt, and from these six others were obtained by dilution. To four portions of these solutions of each concentration, there was added an excess of finely divided iodine; and the mixtures were then rotated in bottles with glass stoppers in a thermostat at 25°, by means of the earlier described apparatus.[1] Duplicate determinations were always made in such a way that the state of saturation was approached both from a higher and from a lower temperature. Furthermore, each pair of determinations was checked by a second, in which fresh solutions prepared by weighing out the iodide anew were used. After the bottles had been rotated from four to five hours, the solutions were allowed to stand over night to settle; twenty-five or fifty cc. were then pipetted out, and the dissolved iodine was titrated by means of sodium thiosulphate with starch as an indicator. In determining the solubility in water, particular regard was paid to the purity of the water, which was distilled from alkaline permanganate, and proved pure by measur-

[1] *Ztschr. phys. Chem.*, 9, 606.

ing its conductivity. In order to detect any slight influence due to the formation of hydriodic acid, the bottles were rotated in the thermostat during different lengths of time; but no difference in the results could be detected.

The following table contains the results in millimols, or thousandths of a molecular weight, per liter. Under the heading "undersaturated", the values are given which were obtained by warming from a lower temperature up to 25°, while under "supersaturated", those appear which were obtained in the opposite way.

SOLUBILITY OF IODINE.

	Millimols of dissolved iodine (I_2) per liter.				
Millimols of KI per liter.	Undersaturated. I.	II.	Supersaturated. III.	IV.	Mean.
106.3	55.20	55.39	55.14	55.38	55.28 ±0.05
53.15	28.03	27.97	28.16	27.96	28.03 ±0.03
26.57	14.70	14.65	14.72	....	14.68 ±0.02
13.29	8.018	7.992	7.998	8.003	8.003±0.004
6.643	4.678	4.712	4.589	4.688	4.667±0.019
3.322	3.138	3.061	2.906	3.102	3.052±0.036
1.661	2.223	2.214	2.241	2.262	2.235±0.008
0.8304	1.830	1.838	1.779	1.809	1.814±0.010
0	1.363	1.347	1.465[1]	1.283[1]	
0	1.302	1.337	1.341	1.357	
0	1.333	....	1.329	1.351	1.342±0.004[2]
0	1.343	....	1.360	....	

An inspection of the table shows that no regular difference exists between the "undersaturated" and the "supersaturated" values, which proves that the solutions had reached the state of equilibrium. The degree of concordance of the single results is best shown by the values of the deviations from the mean in the last column. From the results with pure water, it is obvious that the amount dissolved was independent of the time during which the bottles were rotated. The solubility found (1.342 millimols) agrees also well with that obtained by Jakowkin (0.3387 gram or 1.335 millimols per liter).

In order now to test the application of the law of mass action, we must first of all subtract from the total amount of dissolved

[1] Omitted in the calculation of the mean.

[2] In determining the amount of iodine necessary to saturate pure water, the bottles were rotated during different lengths of time; namely, as follows: first series, two hours; second series, four hours; third series, one day; fourth series, seven days.

iodine, the amount of iodine soluble in pure water. In this way, the amount of iodine is found which is present in the form of the complex salt; and, if the ratio of this quantity to the total amount of potassium iodide is calculated, it can be seen at once to what extent the simple proportionality exists which the law of mass action requires in case only the compound KI_3 is formed. The results (expressed in millimols) of this calculation are arranged in the following table:

$KI+KI_3$.	$KI+I_2$.	KI_3.	Ratio. $KI_3 : (KI+KI_3)$.
106.3	55.28	53.94	0.5074
53.15	28.03	26.69	0.5021
26.57	14.68	13.34	0.5021
13.29	8.003	6.661	0.5012
6.643	4.667	3.325	0.5005
3.322	3.052	1.710	0.5148
1.661	2.235	0.893	0.5376
0.8304	1.814	0.472	0.5684

It is evident from the last column of this table that between the concentrations 0.1 and 0.006 normal the iodine present in the form of a complex salt is closely proportional to the total quantity of potassium iodide. In the case of the more dilute solutions, however, the relation of these two quantities seems to increase; but this is probably to be attributed to experimental error, for the quantity of iodine present as complex salt is less in these cases even than the solubility in pure water. Aside from these very dilute solutions, the assumption that the iodine exists exclusively as free iodine and as a constituent of the salt KI_3 (or of its anion) is therefore in complete accord with the law of mass action. The conclusion of Jakowkin in regard to the constitution of the complex salt is thus confirmed by the solubility relations.

THE NATURE OF VALENCE.

[SECOND PAPER.]

BY F. P. VENABLE.

Received January 23, 1899.

AS the preceding paper upon this subject was in the form of an address before one of the local sections of the society, the hypothesis as to the cause of valence there suggested was given in outline only and could not be enlarged upon as far as

may have been necessary. In the present paper it is proposed to elaborate certain points and to test, as far as possible, the reasonable nature of the hypothesis.

While the whole subject of valence has been much confused, and the use of some of the terms connected with it unfortunate, no part of it has given greater trouble than its variability. This is the very point, however, which affords the best clew to its solution and should therefore be treated at some length.

The most instructive cases of varying valence are those where the variation is shown towards the same element, as in the compounds PCl_3 and PCl_5, $FeCl_2$ and $FeCl_3$, Hg_2O and HgO, CO and CO_2, and many other similar compounds. There are two possible views regarding these. Either the valence varies or the valence remains the same and the differences are explained by some such assumption as that of a state of saturation of the atom and of various unsaturated states.

The terms 'saturated' and 'unsaturated' present a number of anomalies as commonly used. In the first place the term saturated is not always used for that condition of the atom in which it is united with the largest number of other atoms. Thus, ferrous oxide (FeO) is called unsaturated, and ferric oxide (Fe_2O_3) saturated, though there is a larger proportion still of oxygen in ferric acid and the ferrates. The same is true of the three series of manganese and chromium compounds.

Again the term saturated does not carry with it any definite relation to the stability of the compound. Sometimes the compound called unsaturated, and containing the least number of atoms is the most stable, sometimes that with the largest number. Phosphorus trichloride is more stable than the pentachloride, but the pentoxide is more stable than the trioxide. The most stable of the manganese compounds are the so-called unsaturated manganous salts; in the case of chromium it would appear to be the chromic salts. In the case of carbon the saturated compounds are the most stable. It is manifest that these two terms cannot cover all cases of combination for a number of elements. It would seem wiser and simpler then to speak of the valence directly when discussing the elements, as bivalent carbon or quadrivalent carbon; bivalent or trivalent iron, etc. In the case of carbon compounds the terms have acquired a

somewhat different meaning and are too thoroughly incorporated in the literature for a change to be suggested. Saturated here means a compound which can take on no further atoms by addition, while an unsaturated compound can have such atoms added.

Certain cases of change of valence, as in cuprous and cupric compounds, mercurous and mercuric, ferrous and ferric, etc., have been looked upon as presenting some peculiar relationships. Such cases are spoken of by some as if they occurred among positive elements only. It is not clear how any distinction can be drawn between these and the classes phosphorous and phosphoric, sulphurous and sulphuric, nitrous and nitric, chlorous and chloric, etc. A possible distinction might be made that the more negative the element the greater the number of changes of valence; the more positive the element the less variation in valence is observed. This would be an approximation only.

So great is the difference caused by this variation in the valence that some have even thought it best to arrange what have been called the lower and higher stages under different groups. Thus Mendeléeff placed cuprous copper in Group I, and cupric copper in Group VIII; aurous gold in Group I and auric gold in Group VIII. Such an arrangement would, however, greatly confuse the periodic system. Mercury, thallium, chromium, manganese, phosphorus, arsenic, sulphur, selenium, and others would have to be similarly provided for. It is better to retain them in the positions to which their atomic weights would assign them and to study them more thoroughly, so that we may understand why certain elements, as copper, gold, and mercury show this peculiarity while others closely akin to them, as silver, zinc, and cadmium, do not. In studying the nature of valence from the standpoint of its variability, the means by which these variations can be brought about must have an important bearing upon the subject. There are a number of these agencies.

Light.—It is a matter of common observation that light can bring about physical, and the most varied chemical, transformations. In some cases it is apparent that the transformation is one from a higher to a lower valence or *vice versa*. Thus, certain mercurous compounds can be changed to mercuric.

$$Hg_2O = HgO + Hg.$$

An alcoholic solution of ferric chloride is changed by light to ferrous chloride.

$$2FeCl_3 + C_2H_6O = 2FeCl_2 + C_2H_4O + 2HCl.$$

Ferric oxalate under the influence of light gives off carbon dioxide and becomes ferrous oxalate.

$$Fe_2(C_2O_4)_3 = 2Fe(C_2O_4) + 2CO_2.$$

An alcoholic solution of cupric chloride becomes cuprous chloride. Mercuric chloride in aqueous solution is slowly changed to mercurous when exposed to the light.

$$2HgCl_2 + H_2O = 2HgCl + 2HCl + O.$$

Gold chloride ($AuCl_3$), in contact with organic substances, when exposed to light, is changed first to aurous chloride ($AuCl$) and then to metallic gold.

It is quite well known that a ray of light falling upon a piece of selenium changes its conducting power for electricity. This is not a change of valence but has, it would seem, its bearing upon the problem as a possible change in vibration. The chemical action of light is generally attributed to the vibrations set up among the molecules. Rays having the shortest wave-lengths and the greatest frequency are most active in this respect though all the rays of the visible spectrum have been shown to exert some action. So far as this variation in valence is caused by light then the hypothesis of a change in vibration necessitating a change in equilibrium may well serve as an explanation.

Heat.—Again these variations are often easily brought about by changes of temperature. Thus cupric chloride becomes cuprous chloride.

$$CuCl_2 = CuCl + Cl.$$

Mercurous chloride is temporarily changed into mercuric, the mercurous re-forming upon cooling.

$$2HgCl = Hg + HgCl_2.$$

Phosphorus pentachloride becomes the trichloride.

$$PCl_5 = PCl_3 + Cl_2.$$

Arsenic pentoxide becomes trioxide.

$$As_2O_5 = As_2O_3 + O_2.$$

An interesting series of changes are those in the sulphur chlorides. Thus sulphur tetrachloride (SCl_4) becomes sulphur

dichloride (SCl_2), if warmed above —22°, and this becomes sulphur monochloride (S_2Cl_2), if heated above 64°. This last can be boiled without change.

These instances might be multiplied but it is not necessary. The most plausible explanation offered as to the effect of heat is a change in the velocity of vibration, and it may well serve to explain the variations caused in valence.

Electricity.—Changes of valence due to electricity are probably not unusual but few observations concerning them have been recorded. One of the most noteworthy is the production of carbon monoxide from carbon dioxide by the passage of the electric spark.

$$CO_2 = CO + O.$$

Chemical Action.—The most usual method of bringing about a change of valence is by chemical action. When the change is from a higher proportion of the negative element to a lower it is commonly called *reduction*, and the reverse change is spoken of as *oxidation*. These terms are apparently relics of an older theory, and are confusing, especially to a student beginning the study of chemistry. They should be limited to cases of the actual removal or addition of oxygen. Thus, to speak of the change of ferrous to ferric chloride by the action of chlorine as an oxidation is careless and incorrect.

$$FeCl_2 + Cl = FeCl_3.$$

It is pushing the type theory rather far to speak of the salts of one valence as being derived from the oxide of that valence and yet this is frequently done.

When we take ferric chloride and let sulphurous acid act upon it, it is called a reduction of the ferric chloride to ferrous chloride, although certainly no oxygen is removed from the ferric chloride nor is oxygen added when the ferrous chloride is changed again to ferric chloride by the action of nitric acid, and still this is called an oxidation. The use of terms for these reactions is evidently in need of revision. What shall we call the following reaction, cited by Drechsel as an "oxidizing action?"

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Some hydrogen is oxidized with the formation of water but that

is not what is meant. The manganese is changed from its highest valency to its lowest and the iron from its lowest to a higher. The permanganate is of course deoxidized.

It seems that chemical action may induce change when to an existing molecule a third substance is offered capable of combining with one or more of its constituent atoms, thus releasing the former equilibrium. Thus when sulphurous acid takes the oxygen of water setting hydrogen free the hydrogen then takes one of the chlorine atoms held by the iron.

$$2FeCl_3 + H_2SO_3 + H_2O = H_2SO_4.2HCl + 2FeCl_2.$$

But the presence of all three of these molecules is needed for the reaction to take place. So too, potassium permanganate is stable in the presence of sulphuric acid, unless the ferrous sulphate or some such molecules are present. When molecules of these three substances come together there is immediate rearrangement of molecules with change of equilibrium. Whether we are dealing here with a play of affinity which causes the tumbling down of certain molecules and building up of others, or whether it is a question of vibratory equilibrium between these molecules, cannot yet be told. The only certain thing seems to be that a molecule containing bivalent iron and another containing septivalent manganese cannot exist in the presence of one another but must change, when possible, to trivalent iron and bivalent manganese.

As meagre as our present knowledge is, it does not seem to be a very hopeful task to enter the maze of changes of valence through chemical reactions with a view to clearing up the ideas as to the nature of valence.

Explanations Offered.—Victor Meyer and Riecke have supposed that a solution of the problem could be arrived at best by studying the phenomena of frictional electricity, contact electricity, pyro-electricity, and electrolytic conductivity. Most of those who have suggested hypotheses have based them upon a study of the carbon atom and its compounds and in particular its space relations. I have gathered together such of these hypotheses as have come to my notice and for fear of doing the authors an injustice shall present their views as far as possible in the original language.

The first in point of time is the hypothesis of van't Hoff.[1] I have not had access to the original but will give van't Hoff's views as presented by Rössing and by Ostwald. Rössing[2] quotes:

"Die einfachste Betrachtung lehrt, dass jede Abänderung von der Kugelgestalt zu grösseren Äusserungen der Anziehung nach bestimmten Richtungen führen muss, da sich das Atom an diesen Stellen so zu sagen besser annähern lässt. Jede derartige Form bedingt also eine gewisse Zahl Hauptanziehungsfähigkeiten, Valenzen.

"Wo nun obendrein noch die Art des gebundenen Atoms die Bindungskraft bedingt, wird auch die Zahl der hervortretenden Valenzen davon abhängig sein, somit beim Vergleich der Verbindungen eines bestimmten Elementes mit verschiedenen anderen öfters eine Änderung der Valenz auftreten.

"Wenn sich ein Atom um eine bestimmte Lage gleichmässig in allen Richtungen hin und her bewegt, ist eine Änderung der äusseren Form, somit auch von Affinität und Valenz, notwendige Folge.

"Zieht man jetzt in Betracht, dass die Schwingungsgrösse der Atombewegungen von der Temperatur bedingt wird, so führt obige Anschauung zu dem thatsächlich gestützten Schlusse dass Temperaturzunahme die Anzahl der Valenzen verkleinert, die Affinitätserscheinungen abschwächt, also die gegenseitige Atomwirkung allmählich zur einfachen Gravitationsäusserung zurückführt. Thatsache ist, dass es eine obere Temperaturgrenze gibt, wobei von chemischer Wirkung nicht mehr die Rede ist; Thatsache ist auch, dass im entgegengesetzten Falle die chemischen Erscheinungen sich ungeheuer komplizieren, zweifelsohne dadurch, dass bis dahin ubersehene Valenzen zur Geltung kommen.

"Die aufgestellten Betrachtungen ergeben als unmittelbare Folge, dass eine Atomvereinigung, ein Molekül, sich anderen gegenüber in der nämlichen Art und Weise, nur weniger scharf, äussert, wie das Atom selbst; auch das Molekül hat Affinität und Valenz, die zwar durch die eigenthümliche Zusammenstellung der Theile bedingt, nicht aber letzteren an und für sich eigen sind. So ergibt sich eine Grundlage für die Betrachtung der so-genannten Molekularverbindungen."

[1] Ansichten über die organische Chemie, I, 3.
[2] Rössing: Theoretische Chemie, 180.

Ostwald[1] comments upon this hypothesis as follows :

" Es bleibt indessen noch eine Möglichkeit, die thatsächliche Verschiedenheit der Valenzwirkungen zu erklären. Wenn wir die Valenz als Frage einer Eigenschaft der Atome auffassen, deren Wirkung durch die Verschiedenheit der Zustande des Atoms insbesondere der Bewegungszustande, modifiziert werden kann, so ist es denkbar, dass obwohl die Ursache der Valenz unveränderlich ist, die Wirkungen dieser Ursache, eben die Valenz selbst, von Fall zu Fall verschieden erscheint.

" Eine Hypothese der erwähnten Art ist in der That von van't Hoff aufgestellt worden. Indem er annahm dass die chemische Anziehung zwischen den Atomen eine Folge der Gravitation sei, zeigte er, dass wenn ein Atom eine von der Kugelgestalt abweichende Form besitzt, die Intensität der Anziehung auf seiner Oberfläche eine bestimmte Anzahl Maxima besitzen müsse welche von der Form abhängt. Die Maxima können von verschiedenem Werte sein. Ist die Wärmebewegung des Atoms eine lebhafte, so werden nur die grösste Maxima ihre Atome festhalten können, und die Valenz zeigt sich, entsprechende der Erfahrung, bei höherer Temperatur kleiner als bei niederer."

Lossen's[2] idea as to valence, deduced from the consideration of the theories of van't Hoff and Wislicenus as to the space relations of the atom seem to be condensed into the single sentence:

" Diese Auffassung führt, nach meiner Meinung, nothwendig zu der Annahme, dass das mehrwerthige Atom sich überhaupt nicht als materieller Punkt betrachten lässt, dass vielmehr Theile desselben zu unterscheiden sind, von welchen die Wirkung auf andere Atome ausgeht."

Wislicenus[3] expresses his ideas as to valence as follows :

" Ich halte es nicht für unmöglich, dass das Kohlenstoffatom ein Gebilde sei, welches in seiner Gestalt einem regulären Tetraëder mehr oder weniger vielleicht recht sehr ähnelt : nicht für unmöglich ferner, dass die Ursachen jener Wirkungen, welche in den 'Affinitäts-einheiten' zur thatsächlichen Erscheinung kommen, sich in den Ecken dieses tetraëdrischen Gebildes concentriren, möglicherweise ähnlich und aus analogen Gründen, wie dies die elektrischen Wirkungen eines elektrisch geladenen

[1] Lehrbuch der allg. Chemie, I ed. I, 830.
[2] *Ber. d. chem. Ges.*, **20**, 3309.
[3] *Ibid.*, **21**, 581.

Metalltetraëders thun würden. Die eigentlichen Träger dieser Energie würden schliesslich die Uratome sein, ganz wie die chemische Energie der zusammengesetzten Radicale unzweifelhaft eine Resultirende der den Elementaratomen innewohnenden Energie ist."

Victor Meyer and Riecke[1] advance the following hypothesis:

"Auf Grund der mitgetheilten chemischen und physikalischen Erfahrungen haben wir uns nun folgende Vorstellung von der Constitution des Kohlenstoffatomes gebildet. Wir nehmen an, dass dasselbe umgeben ist von einer Aetherhülle, welche bei isolirten Atome, wie dieses selbst, kugelförmige Gestalt besitzt; das Atom selbst betrachten wir als den Träger der specifischen Affinitäten, die Oberfläche der Hülle als den Sitz der Valenzen. Jede Valenz denken wir uns bedingt durch das Vorhandensein zweier entgegengesetzter elektrischer Pole, welche in den Endpunkten einer im Vergleich zum Durchmesser der Aetherhülle kleinen geraden Linie befestigt sind. Wir bezeichnen ein solches System zweier elektrischer Pole als einen Doppelpol oder Dipol. Den vier Valenzen des Kohlenstoffatomes würden also vier solcher Dipole entsprechen. Die Mittelpunkte derselben denken wir uns gebunden an die Oberfläche der Aetherhülle, in dieser aber frei verschiebbar; die Dipole selbst seien freidrehbar um ihre Mittelpunkte."

It is scarcely necessary to give the further assumptions. The hypothesis of Knorr[2] may be also given in brief:

"Ich denke mir die Valenzen bedingt durch die Gliederung der Atome in besondere räumlich gesonderte Massen, die ich 'Valenzkörper' nennen will. Jeder Valenzkörper soll die Fähigkeit besitzen, andere Valenzkörper anzuziehen und durch diese Anziehung festzuhalten. . . . Die Werthigkeit ist bestimmt durch die relative Anzahl der in einem Atom vorhandenen Valenzkörper. Die Bindungen kommen zu Stande durch Berührung von Valenzkörpern. Im Kohlenstoffatom müssen die Valenzkörper gleichwerthig und gleichmässig im Raume gruppirt sein."

Flawitzky[3] takes as a basis for his hypothesis the suggestion of N. Beketoff that the cause of the chemical interaction of the

1 *Ber. d. chem. Ges.*, **21**, 951.
2 *Ann. Chem.* (Liebig), **279**, 202.
3 *Zischr. anorg. Chem.*, **12**, 182.

elements lay in the interference or coincidence of the motions of the atoms. The chief assumption is that the atoms of each element described closed curves which lie in planes, which are parallel to one another and have a constant absolute position in space. The atoms of different elements move in planes which make definite constant angles with one another. "Nehmen wir in der That an, dass die lebendige Kraft der Atome verschiedener Elemente gleich gross ist, so kann die Bewegung eines Atomes eines Elementes nur dann durch die Bewegung eines Atomes eines anderen Elementes vollständig aufgehoben werden, wenn die beiden Bahnebenen unter einander parallel sind. Widrigenfalls können je nach der Grösse des Winkels zwischen den Bahnebenen Fälle vorkommen, wo ein Atom eines Elementes dazu zwei, drei und mehr Atome eines anderen verlangen wird. Es können nämlich in solchen Fällen nur diejenigen Komponenten zur Wirkung kommen welche der Bewegungsebene des anderen Atoms parallel sind. Somit lässt sich die Wertigkeit der Elemente auf die Verschiedenheit der Winkel zwischen den Bahnebenen verscheidenartiger Atome zurückführen. Die Grössen dieser Winkel müssen augenscheinlich dem Gesetze ganzer rationaler Beziehungen folgen, wodurch die Fähigkeit der Atome, sich in ganzen Zahlen zu verbinden, bestimmt ist."

It is quite possible that other hypotheses as to valence have been formulated but have escaped my notice. These will suffice to give the more recent trend of thought upon the subject. I may state that none of these were known to me when the first paper was sent on for publication as I had not deemed it necessary to look beyond the usual text-books in examining into the literature upon the subject. This statement is not made for personal reasons as that is a matter of small moment, but that there may attach to my hypothesis whatever of value there is in the independent reaching of a conclusion.

It is not pertinent to this paper to discuss at any length the citations just given. But a few words are needed to bring out certain differences and distinctions. In most of them we have the assumption of some peculiar form of energy—an "Anziehungskraft." Flawitzky alone makes no explicit assumption of the kind. Besides this assumed force, which is the point of contention after all, we have various other assumptions of a remark-

able character; *e. g.*, as to the forms of atoms, envelopes, primal atoms, and *Valenzkörper*. Flawitzky's hypothesis is based upon the angles made between the planes in which the atoms move.

Now in the place of all this I wish to substitute that which seems to me to be the simpler hypothesis of vibratory equilibrium.[1] There is only one attractive force to be considered and this is called chemical affinity and causes the union of the atoms, binding them together. These atoms may unite atom with atom, or one atom with two or three or more atoms of the other element or other elements. While we speak of union there is no actual contact to be assumed. The individual atoms have their own motion and at the same time the aggregation of atoms, or molecule, has a motion proper to it. The conditions of equilibrium in such a system determine the number of atoms which can enter it: as one to one, one to two, etc. There is no distinct force of valence determining this. The form of the atoms can scarcely be taken into consideration because the distance between the atoms is too great, compared with the mass of the atom, for the form to exert much influence, unless it influences the character of the motion. The atomic weight also has little influence in determining the number of atoms needed to satisfy the conditions of equilibrium except that there seems to be a general rule that with increase in the atomic weight in any one group more stable equilibrium is brought about with the smaller number of atoms and in a choice between several the lesser valence is preferred. (Compare nitrogen and bismuth; sulphur and tellurium.)

There would then appear to be seven, possibly eight, different kinds of motion among the atoms. Different velocities of vibration are not meant, but different phases of motion. For instance, all may have elliptical orbits with different focal distances; or circular, with different radii, etc. In any group of elements the motion of the atoms would have one common characteristic but there would be differences in velocity. In the first and seventh group, showing, for the most part, a tendency towards the same equilibrium, or having the same valence, the motion must be closely analogous. So too for the second and sixth groups, the third and fifth. There may then be a necessity for four distinct

[1] Dr. Jas. Lewis Howe suggests the name "kinetic equilibrium."

phases only, unless we suppose a fifth for the eighth group. If the motion of an atom can be changed from one character to another its valence is changed and in such general properties as are dependent upon motion and not upon atomic weight it is equivalent to changing its group. Electricity, light, heat, and chemical action can cause this change of motion. In so far the properties of the element are subject to change and within our control. But the other factor, atomic weight, with the properties of the element determined by it, is not subject to change nor within our control, so far as our knowledge goes.

While it is freely granted that there is so much of the speculative in what has been said as to make us touch the whole subject with extreme caution, and while it is further admitted that it is quite beyond the reach of present experimental research, yet it is believed that the use of the imagination is legitimate and tends toward the advancement of the science so long as the true value is set upon it and fancy is not allowed to obscure fact nor to be mistaken for it. The hypothesis proposed is simple and if true will be very helpful. It will be a great step forward if it can be shown that the doctrine of valence is a doctrine of vibratory equilibrium.

EMETINE OCTOIODIDE AND THE EXTRACTION AND ESTIMATION OF ALKALOIDS GENERALLY.[1]

By H. M. Gordin and A. B. Prescott.

Received November 27, 1898.

IN a previous paper[2] we have shown that most alkaloids form definite compounds when treated with excess of iodopotassium iodide and that it is possible to estimate the strength of aqueous solutions of alkaloidal salts by means of standardized solutions of iodine and of sodium thiosulphate. In applying this method to the assay of medicinal drugs it is immaterial what method of extraction of the alkaloids from the drug is employed, provided the final alkaloidal solution be sufficiently deprived of non-alkaloidal matter. The simplest and quickest method of obtaining the alkaloidal solution sufficiently free from foreign

[1] In the work of Research Committee D, Section 2, Committee of Revision and Publication of the Pharmacopoeia of the United States. Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

[2] This Journal, **20**, 706, Sept., *1898*.

matter is undoubtedly the method proposed by Dr. A. B. Lyons.[1]

This consists in macerating a weighed quantity of the powdered drug in a definite volume of Prollius' fluid with frequent shaking for several hours, drawing off an aliquot part of the clear liquid, evaporating and taking up the residue with acidulated water. The alkaloidal solution obtained by this method is generally almost perfectly colorless and can be worked up further for a gravimetric estimation by shaking out the alkaloids with chloroform and ammonia. For our iodometric method the filtered solution can be treated directly with excess of iodine, the excess of which is then estimated by sodium thiosulphate. For the alkalimetric estimation, again, the same filtered solution may be taken, using standardized acid in excess and estimating the excess by means of standardized alkali. The only drawback to this method of extraction is the great difficulty of preventing loss by evaporation of the highly volatile solvent, by which loss the volume of the aliquot part becomes reduced, and the final figure is liable to be too high.

A GENERAL METHOD OF EXTRACTION.

In order to avoid this difficulty we have worked out an entirely different method of alkaloidal extraction which can also be used with any one of the methods of estimation as desired. In its main features this method is the same as that which we proposed for the assay of opium.[2] It is carried out in the following manner :

One to four grams of the finely powdered drug is weighed into a low wide-mouthed vessel, with a round bottom, holding eight or ten ounces and having a well-fitted cork, such as a screw-top ointment-jar.[3] The powder is rubbed up with a small pestle to a fine paste by adding a little of a solvent mixture, composed of stronger ammonia water and alcohol each five cc., chloroform ten cc., and ether twenty cc. Then a few more cubic centimeters of this mixture are added, so as to have the drug well covered with the liquid, using in all about five times the amount of the drug taken. The vessel is corked, with the pestle inside, and is set aside for about four or five hours, taking care to agitate by

[1] Manual of Pharm. Assaying, Haynes & Co., Detroit, Mich., *1886*, p. 20.
[2] This Journal, *1898*, **20**, 724; *Pharm. Archives*, *1898*, p. 121.
[3] An ordinary teacup fitted with a specie cork answers well.

circular movement very frequently during that interval. After that time the cover is removed and the vessel kept in a current of air, stirring frequently till all odor of ammonia has disappeared. With a good draught and frequent stirring the powder will be almost perfectly dry in about two hours. The vessel is then put into a vacuum desiccator over sulphuric acid for about four or five hours.

An amount of powdered sodium chloride equal to about five or six times the amount of drug employed is then carefully mixed in, with use of the pestle, and the whole thrown into a small percolator, one provided with a glass stop-cock and having a plug of cotton at the bottom.[1] The vessel is then cleaned out several times with small quantities of sodium chloride, and the cleanings added to the percolator. The mixture in the percolator is then covered with a piece of cotton which is pressed down with a piece of glass, and a suitable menstruum, usually chloroform, is poured slowly into the percolator till the menstruum reaches the stop-cock. The latter is then closed, the percolator covered, and set aside for five or six hours. After that time the stop-cock is opened, and the drug exhausted with the menstruum percolating until ten drops of the percolate being evaporated on a watch-glass, and the residue taken up with a few drops of acidulated water, the solution shows no turbidity whatever on adding a few drops of Wagner's reagent. When finished the percolate, which is received in a flat evaporating dish, is placed in a good draught at a temperature of about 30° C. When the liquid is reduced to a very small volume, ten cc. of acidulated water[2] are added, and then a few cubic centimeters of ether, or petroleum ether, so as to have an ethereal liquid cover the aqueous solution,[3] when the whole is stirred with a glass rod until all the ethereal liquid is driven off. The liquid is then filtered and the evaporating dish and filter washed several times with acidulated water. In this way is obtained a colorless solution of the alkaloid, which can be worked up for any method of assay.

[1] A suitable percolator is easily made out of an ordinary piece of glass tubing fitted with a perforated cork through which passes a tube having a glass stop-cock.

[2] If an alkalimetric assay is intended the acidulated water in the operation should be standardized and taken in definite quantities.

[3] If the menstruum is all evaporated off it is sometimes difficult to dissolve out the alkaloids with acidulated water. If chloroform be used, coming below the aqueous layer, it evaporates too slowly.

THE IODOMETRIC ESTIMATION.

In the periodide method of assay the final alkaloidal solution obtained, whether by our method, by Dr. Lyons' method, or by any other method, this final solution representing a definite quantity of the drug to be assayed, is poured slowly and with constant stirring into a flask holding 100 cc. in which has been previously drawn twenty or thirty cc. of a standardized solution of iodine and one or two cc. of dilute hydrochloric acid[1] (U. S. P.). The flask is then filled up to 100 cc., stoppered, and well shaken till the periodide has separated out. The supernatant liquid is to be perfectly transparent but of a red iodine color. Fifty cc. are then filtered off and in this portion the excess of iodine determined by means of standard sodium thiosulphate. The amount of iodine consumed multiplied by the suitable factor, gives the amount of alkaloid present in the quantity of drug taken.

In the case of several alkaloids being present in the drug a mean iodometric factor can be deduced in the same way as is done in the alkalimetric assay. It is to be noticed that should there be no precipitate with iodine, but only a slight turbidity, then the drug is extremely poor and for the assay a much larger quantity than one to four grams should be taken. On the other hand should the supernatant liquid, after adding the alkaloidal solution to the iodopotassium iodide solution and separating the periodide by shaking, have very little color or be almost colorless then it is certain that the drug is very rich, and either a smaller quantity of the drug or a larger quantity of the iodine solution must be employed in the assay.

The method of extraction described above presents particular advantages in those cases where several alkaloids soluble in different menstrua are present in the drug, as by using these menstrua successively, a separation of the alkaloids can be easily effected. This principle we have applied to the assay of opium, and it seems also to be applicable to *Hydrastis canadensis*, a report upon which we intend to publish in the near future.

This method of extraction of alkaloids for assay purposes has given us very good results with all drugs experimented upon,

[1] Except in the case of morphine an excess of acid is not hurtful and even promotes the separation of the periodide. Hydrochloric is to be preferred to sulphuric acid.

except ipecac root. For some unaccountable reason it is almost impossible to extract free emetine, which is liberated in our process by the ethereoammoniacal mixture, from this root by percolation. Ether, chloroform, and acetone were tried as menstrua, but in all cases the result was much lower than that obtained by Lyons' process.[1] Though the percolation was not interrupted till a few drops tested in the general way with Wagner's reagent gave no reaction whatever. The very low result as compared with that obtained by Lyons' method shows conclusively that the exhaustion cannot be made complete by percolation. This fact would possibly explain why Flückiger[2], who extracted ipecac by percolation with ammoniated chloroform, obtained exceptionally low results.[3] In the assay of ipecac, given at the end of this paper, the method used was that of Dr. Lyons. The other drugs have been extracted by our method as described above, and the results compared with those obtained by Lyons' method.

The periodide assay method applied to nux vomica, along with a modification of Dunstan and Short's method of separation of strychnine from brucine[4] affords a convenient way of separate estimation of each of these alkaloids in the drug as follows:

The acidulated alkaloidal solution obtained from nux vomica in any suitable way, and representing four grams of the drug, is made up to a definite volume, say 100 cc. Of this solution twenty-five cc., which represent one gram of nux vomica, are run from a burette into a 100 cc. flask in which has been placed twenty cc. of decinormal iodine solution and two cc. dilute hydrochloric acid, and the amount of iodine consumed by the total alkaloids contained in that one gram nux vomica is reached in the way described above. Let that amount be *a*. If only the amount of total alkaloids in the nux vomica is desired it is sufficient to multiply *a* by 47.845 which is equal to 100 times the mean factor of strychnine and brucine and the percentage of total alkaloids is at once obtained.

THE SEPARATE ESTIMATION OF STRYCHNINE AND BRUCINE.

For the separate estimation of each of these alkaloids, another

[1] It is Lyons' general method, not his modification of Dragendorff's method, that is referred to here.

[2] *Pharm. Ztg.*, *1886*, 30.

[3] See also Guareschi: Einfeuhr in d. Stud. d. Alkal., *1896*, 527.

[4] *Pharm. J. Trans.* (3), 14, 290; *Am. J. Pharm.*, *1883*, 579.

portion of the alkaloidal solution, representing two grams of the nux vomica, that is fifty cc., is run out from the burette into an Erlenmeyer flask of the capacity of about 300 cc. and to the contents of the flask ten cc. of a two per cent. solution of sulphuric acid is added, and then water enough to make in all about 200 cc. Then pour in twenty-five cc. of a five per cent. solution of potassium ferrocyanide, stopper the flask and shake continuously for about half an hour. Now filter, wash the precipitate on the filter repeatedly with water containing one per cent. of sulphuric acid, till a few drops of the filtrate diluted with a little water have no bitter taste. The filter is then pierced and the precipitate rinsed with use of the wash-bottle into a 100 cc. flask. To the contents of the flask are then added twenty cc. of a five per cent. solution of zinc sulphate, and the flask kept on a boiling water-bath for about fifteen minutes. The zinc sulphate decomposes the strychnine ferrocyanide, zinc ferrocyanide is precipitated, and strychnine sulphate remains in solution. The flask is then completely cooled, and water enough added to make 100 cc. Of this, fifty cc. representing again one gram of the nux vomica but deprived of the brucine, are then filtered off and run out from the burette into a 100 cc. flask containing twenty cc. decinormal iodine solution, and about two cc. of dilute hydrochloric acid. The amount of iodine consumed by the strychnine alone is then determined as above. Let it be b. Then $b \times 43.9$ (100 times the strychnine factor) gives the percentage of strychnine, and $(a - b) \times 51.79$ is the percentage of brucine in the nux vomica.

To test the exactness of this method we prepared a solution containing known quantities of each of these alkaloids and determined these by the described method. The results as can be seen from the following table are fairly satisfactory, if we consider the well-known difficulties of this separation.

The solution contained 0.16 per cent. strychnine and 0.22 per cent. brucine (anhydrous).

	Iodine consumed by 10 cc. before the removal of brucine.	Iodine consumed by 10 cc. after the removal of brucine.	Found. Strychnine.	Found. Brucine.	Contained. Strychnine.	Contained. Brucine.
1	0.0843132	0.032397	0.14	0.24	0.16	0.22
2	0.0843130	0.032397	0.14	0.24	0.16	0.22

Following is a report of drugs which we have so far assayed

both gravimetrically and iodometrically. The factors are those given for the higher periodides in our previous paper.[1] For nux vomica the mean factor was taken which is equal to 0.47845 parts of total alkaloids for one part iodine consumed. For ipecac root the factor 0.5453 is used which is based upon the fact that, as shown at the end of this paper, emetine forms a hydriodide heptiodide when treated with excess of iodopotassium iodide.

Taking Lefort and Wurtz's formula for emetine we get

$$7 \times 126.53 : 482.98 :: 1 : \text{factor} = 0.5453.$$

The factors for the drugs of the table are as follows:

Mean factor of strychnine and brucine	0.47845
Atropine	0.2849
Emetine	0.5453

Drug.		Quantity taken for assay. Grams.	Iodine consumed.	Percentage of alkaloids. Iodometric.	Gravimetric.
Nux Vomica.					
Iodometric	1	1	0.0526816	2.52	....
	2	1	0.0526725	2.52	....
Gravimetric	1	1	*	....	2.73
	2	1	*	....	2.73
Belladonna Root.					
Iodometric	1	2.5	0.0459179	0.52	....
	2	2.5	0.0459263	0.52	....
Gravimetric	1	2.5	*	....	0.51
	2	2.5	*	....	0.51
Belladonna Leaves.					
Iodometric	1	5	0.0478286	0.27	....
	2	5	0.0475922	0.27	....
Gravimetric	1	5	*		0.28
	2	5	*		0.28
Ipecac Root.					
Iodometric	1	2	0.0957764	2.61	....
	2	2	0.0986633	2.69	....
Gravimetric	1	2	*		2.63
	2	2	*		2.62

* Alkaloids shaken out and weighed.

Emetine Octoiodide.

Emetine seems to form with iodine two periodides, according to whether the iodine is added to the alkaloid or *vice versa*, but owing to the lack of material we have only isolated and analyzed

[1] This Journal, (*1898*), **20**, 724.

one; namely, the higher periodide. The emetine used was obtained from Merck & Co. The periodide was made by pouring 200 cc. of a solution of emetine in acidulated water, this solution containing about half a per cent. of the alkaloid, into about 500 cc. of a solution which contained about one per cent. of iodine with one and five-tenths per cent. of potassium iodide, and was strongly acidulated by hydrochloric acid. The mixture was shaken till the supernatant liquid became perfectly transparent, the precipitate was separated by means of the pump, quickly washed with cold water and then dried, first on porous plates and then *in vacuo* over sulphuric acid.

Thus obtained the periodide is a dark-brown powder, hardly soluble in benzene, ether, or chloroform, quite soluble in alcohol, and very soluble in a mixture of four parts of alcohol and one of chloroform. The chloroform greatly increases the solubility of the periodide in alcohol, though chloroform alone hardly dissolves it. So far we have not been able to recrystallize it. On evaporation of the solvent a viscous mass is generally left. Authorities differ with regard to the formula of emetine, as follows:

Lefort and Wurtz,[1]	$C_{28}H_{40}N_2O_5 = 482.98$
Glenard,[2]	$C_{30}H_{44}N_2O_4 = 494.96$
Kunz,[3]	$C_{30}H_{40}N_2O_5 = 506.92$
Paul and Cownly,[4]	$C_{15}H_{22}NO_2 = 247.48$

Our periodide corresponds best to the formula of Lefort and Wurtz. It seems to be an emetine hydriodide heptiodide, $C_{28}H_{40}N_2O_5.HI.I_7$.

For the estimation of the additive iodine the periodide is dissolved in chloroform mixed with alcohol and titrated with standardized sodium thiosulphate using starch as indicator. It is best to add first an excess of the thiosulphate solution, then add considerable water, when the excess is titrated back with standardized iodine. For the total iodine the periodide is dissolved in a little chloroform mixed with a few drops of alcohol; powdered zinc is then added and the mixture kept on a water-bath till effervescence (from the action of zinc on the chloroform)

[1] *Ann. chim. phys.* (5), **12**, 247.
[2] *Ibid.* (5), **8**, 233.
[3] *Arch. d. Pharm.*, **225** (*1887*), 461; **232** (*1894*), 466.
[4] *Pharm. J.*, (3), **24**, 61.

ceases. To the mixture, when cold, ammonia water is added, and the iodine in the zinc and ammonium iodide is estimated exactly as described in the analysis of morphine tetraiodide.[1]

For additive iodine 0.1492 gram of the periodide gave 0.0880045 gram iodine, and 0.122 gram gave 0.0727250 gram iodine.

	Calculated for $C_{28}H_{40}N_2O_5.HI.I_7$.	Found.
1	59.24	59.98
2	59.24	59.61

For total iodine 0.1313 gram of the periodide gave 0.0890502 gram iodine, and 0.12095 gram gave 0.0818797 gram iodine.

	Calculated for $C_{28}H_{40}N_2O_5.HI.I_7$.	Found.
1	67.69	67.82
2	67.69	67.69

CHEMICAL LABORATORY OF THE
UNIVERSITY OF MICHIGAN,
November 6, 1898.

NOTES ON THE RAPID DETERMINATION OF TUNGSTEN IN STEEL.[2]

BY GEORGE AUCHY.

Received November 3, 1898.

THE rapid method of determining tungsten in steel, generally in use and described in Blair's "Chemical Analysis of Iron," is as follows: Solution of the steel in aqua regia; evaporation to dryness; re-solution in strong hydrofluoric acid containing a little strong nitric acid; dilution and boiling; filtration and ignition of the tungstic oxide contaminated with silica and ferric oxide; elimination of the silica by hydrofluoric acid; ignition and weighing of the tungstic acid and ferric oxide; fusion with sodium carbonate; solution and filtration to determine the ferric oxide. If in this method the final steps—the fusion with sodium carbonate and the determination of the ferric oxide—could be dispensed with, evidently a very considerable saving of time and trouble in the performance of the method would be made; and it has doubtless been observed by many members of the society having occasion to make tungsten determinations in steel, that within the range of their experience the ferric oxide thus carried down with the tungstic acid is constant in amount or nearly so. If this uniformity exists in all steels containing every percentage of tungsten, of course, the determination of

[1] This Journal, *1898*, **20**, 717.

[2] Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

this ferric oxide contamination in every particular instance is unnecessary. One of the objects of this paper is to suggest that if members of the society having to do with tungsten in steel, would gather from their note-books, and publish the data representing the amounts of ferric oxide found contaminating their tungstic acid precipitates, the uniformity of these ferric oxide contaminations would no doubt be shown and result in the improvement of the method. The writer's own experience is confined to steels containing 0.20 per cent. to 1.75 per cent. tungsten, and indicates that the ferric oxide contamination is always practically the same within those limits, and that the amount, with four grams steel[1] taken for analysis and with varying amounts of acid present in solution, is about 0.03 per cent. in terms of tungsten. Results follow :

FIVE CC. FREE HYDROCHLORIC ACID PRESENT IN SOLUTION.

No.	Tungsten. Per cent.	Ferric oxide in terms of tungsten. Per cent.
70	1.110	0.036
504	0.230	0.022
137	1.710	0.032
585	0.250	0.022
352	0.428	0.016
586	0.255	0.022
353	0.434	0.022
587	0.350	0.022
49	1.230	0.032
588	0.375	0.026
51	1.240	0.034
589	0.260	0.028
52	1.240	0.028
590	0.335	0.027
154	1.160	0.028
591	0.310	0.022
346	0.482	0.024
352	0.442	0.020
353	0.434	0.020
363	0.466	0.020
364	0.444	0.020
154	1.090	0.036
380	0.428	0.028
411	0.430	0.026
412	0.400	0.022
179	1.250	0.028

[1] 3.9655 grams. Weight of WO_3 multiplied by twenty gives percentage of tungsten in the steel.

TEN CC. FREE HYDROCHLORIC ACID PRESENT IN SOLUTION.

No.	Tungsten. Per cent.	Ferric oxide in terms of tungsten. Per cent.
179	1.25	0.028
49	1.25	0.028
51	1.25	0.030
52	1.27	0.030
70	1.00	0.028
137	1.65	0.032
154	1.10	0.034
179	1.22	0.042
70	1.08	0.022
352	0.384	0.020
353	0.396	0.020
70	1.100	0.026
179	1.230	0.026
352	0.396	0.028
353	0.390	0.030

More accurately speaking, the amount of ferric oxide contamination lies between 0.02 and 0.03 per cent. for the lower percentages of tungsten and between 0.03 and 0.04 per cent. in steels containing from 1.00 to 2.00 per cent. tungsten. In these tests the ferric oxide in the sodium carbonate used for fusion was found and deducted. Also regard was had for the fact that the weight of the crucible is sometimes slightly affected by the fusion.

Professor Arnold in his "Steel Works Analysis" directs that the tungstic acid be washed with very dilute hydrochloric acid till quite free from iron; and omits the sodium carbonate fusion for the determination of the iron. In the above tests the tungstic acid precipitates were washed seven times with hot hydrochloric acid (1 : 20) and three times with alcohol (1 : 4) filling the filter each time. In one case only 0.10 per cent. tungsten carried down 0.012 per cent. ferric oxide, in terms of tungsten, not washed out by this procedure.

The determination of silicon in tungsten steels is most conveniently made along with that of the tungsten.

PRECAUTIONS IN TUNGSTEN DETERMINATIONS.

Authorities do not agree in considering the completeness of the tungstic acid separation to be affected by the acidity of the liquid from which it separates. For instance, in Blair's

"Chemical Analysis of Iron," the dry residue after the dehydration of the silica is directed to be taken up with an amount of strong hydrochloric acid sufficient for the purpose (about forty cc. for four grams steel, and ten cc. for one gram), and then, without any previous evaporation or neutralization, diluted, boiled, and filtered. In Arnold's "Steel Works Analysis," on the contrary, the liquid is directed to be evaporated to a bulk of five cc. before dilution and filtration. Another point that does not seem to be generally appreciated is that evaporation to dryness and dehydration of silica from nitric acid solution does not always cause complete separation of the tungstic acid, although such an evaporation and dehydration from hydrochloric acid solution will separate all the tungstic acid. In Blair's description of the standard method the evaporation and dehydration is made in nitric acid solution.[1] In Arnold's method the evaporation and dehydration from nitric acid solution is also made, but is followed by a second evaporation to dryness from hydrochloric acid solution, the explanation being made that several evaporations to complete dryness are necessary to insure the complete separation of the tungstic acid on account of its solubility in hydrochloric acid.

With regard to these two points it is the writer's experience that the completeness of the tungstic acid separation is dependent upon the smallness of the amount of acid present in the liquid ; and frequently also upon whether the previous evaporation and dehydration has been made from nitric or from hydrochloric acid solution. The amount of acid in the liquid from which the tungstic acid is filtered should be as little as possible ; and the preceding evaporation to dryness and dehydration of silica should be made in hydrochloric and not in nitric acid solution, in which case only one such evaporation to complete dryness is necessary. The best procedure seems to be : Solution of the steel in dilute nitric acid (taking four grams of the steel); evaporation to first appearance of a scum on the surface of the liquid ; addition of thirty to forty cc. strong hydrochloric acid ; evaporation to dryness and heating on the hot plate; re-solution in forty cc. strong hydrochloric acid ; evaporation to first appearance of scum ; taking up with five cc. strong hydrochloric acid diluted to twenty cc. with water,

[1] In his rapid method the evaporation and dehydration is made from *aqua regia* solution.

and heating; addition of twenty-five to thirty cc. of hot water; and filtration.

The failure of a complete separation of tungstic acid by evaporation to dryness from nitric acid solution is perhaps due to the absence of aqua regia—aqua regia perhaps being necessary to a complete oxidation to tungstic acid. Blair, in fact, in his rapid method, dissolves the steel in aqua regia, and also takes up the dry residue with aqua regia containing, however, an unusual proportion of hydrochloric acid. But this theory is rather discredited by the fact that in Arnold's process no aqua regia is formed, the heating for the dehydration of the silica being carried to the point of decomposition of nitrates, and yet all the tungsten is obtained.

The following results illustrate the necessity for the two precautions just considered.

No.	5 cc. HCl present. Total bulk 50 cc. Tungsten. Per cent.	10 cc. HCl present. Total bulk 100 cc. Boiled before filtration. Tungsten. Per cent.	40 cc. HCl present. Total bulk 100 cc. Boiled before filtration. Tungsten. Per cent.
70	1.11	1.10	1.05
137	1.71	1.67	1.59
352	0.442 0.428	0.396	0.290
353	0.434 0.434	0.390	0.320
49	1.24 1.23	1.24	....
51	1.24	1.25	....
52	1.25 1.24	1.27	....
154	1.16	1.09	....
179	1.26 1.25	1.23	....

In the above tests the filtrates from the tungstic acid of the first column of results were tested for tungstic acid by evaporation to complete dryness with aqua regia. None was found in any test. In the above tests, the evaporations to dryness and the dehydrations of the silica were all made from hydrochloric acid solutions; but in the following determinations they were made from nitric acid solutions.

No.	Tungsten present. Per cent.	Tungsten found. Per cent.
70	1.11	1.08
179	1.26	1.15
352	0.440	0.384
353	0.434	0.396
70	1.11	1.00
137	1.71	1.65
154	1.16	1.10
179	1.26	1.22

But ten cc. hydrochloric acid instead of five cc. were present in the solution; and the lowness of the results may have been partly due to that fact. Comparing results obtained under like conditions as regards the amount of acid present we have:

No.	10 cc. HCl present. Evaporation and dehydration from HCl solution. Tungsten. Per cent.	10 cc. HCl present. Evaporation and dehydration from HNO_3 solution. Tungsten. Per cent.
70	1.10	1.08
179	1.23	1.15
137	1.68	1.65
352	0.396	0.384
353	0.390	0.396
70	1.10	1.00
154	1.09	1.10
179	1.23	1.22

In No. 79 the filtrate from the tungstic acid (1.15 per cent. tungsten) was found to contain 0.10 per cent. tungsten.

Phosphorus in Tungsten Steels.

In Arnold's "Steel Works Analysis" the operator is directed to separate and filter tungstic acid before determining phosphorus. In Blair's "Chemical Analysis of Iron" this is not specified and it is therefore, perhaps, to be inferred that phosphorus is to be determined as usual. The following tests were made, using the volumetric method:

No.	P after separating and filtering tungstic acid. Per cent.	P as usual; yellow precipitate stood less than 2½ hours. Per cent.	P as usual; yellow precipitate stood over night. Per cent.	P carried down by the tungstic acid in the first column of results. Per cent.
154	0.016	0.017	....	0.0007
179	0.025	0.026	0.029	0.0007
70	0.017	0.018	0.024	0.0007
137	0.020	0.023	....	0.0009
70	0.017	0.018	....	....
70	0.017	0.016	....	....
70	0.017	0.018	....	....
154	0.016	0.018	....	....
179	0.025	0.025	0.032	....
179	0.022	0.024	....	....

This indicates that in very low phosphorus steels at least, the determination may be made as usual, provided the yellow precipitate is not allowed to stand more than two and one-half hours. Also in neutralizing with ammonia, no excess must be used or tungstic acid will precipitate with the ferric oxide and remain undissolved by the nitric acid added to clear the solution. But the tendency seems to be toward higher results.

Ferrotungsten

is usually analyzed by roasting, followed by solution, filtration, fusion, and evaporation with acid. The writer, with a sample containing 35.25 per cent. tungsten, obtained low results by this method (twenty-nine and thirty per cent.), doubtless because only a single fusion was made, but had no difficulty when using the same method as for tungsten steels, except that aqua regia was used for a solvent.[1] The ferrotungsten apparently could not be completely decomposed by this means. A bright metallic residue was left, consisting, however, of almost pure tungsten, and readily oxidizing to tungstic oxide by ignition after filtration. In this procedure the preparatory roasting of the ferrotungsten is, of course, unnecessary. The ferric oxide and other contamination seems to be variable; in nine determinations of five different ferrotungstens, it ranged from 0.28 per cent. to 1.60 per cent.

LABORATORY OF THE KEYSTONE SAW WORKS,
PHILADELPHIA, PA.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

THE ABSORPTION OF METHANE AND ETHANE BY FUMING SULPHURIC ACID.[2]

BY R. A. WORSTALL.

Received October 17, 1898.

APPARENTLY one of the most firmly established facts has been that marsh-gas and its homologues are not acted upon either by fuming nitric or by fuming sulphuric acids. The indifference of methane and ethane to all reagents, especially to

[1] The metal being treated first with strong nitric acid and heated, and the strong hydrochloric acid then added by degrees.

[2] Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

fuming sulphuric acid, has been generally accepted as a fact and made a basis for the separation of the saturated from the unsaturated hydrocarbons in gas mixtures. Hempel, in his well-known book on gas analysis, states that no absorbent for methane is known; and a statement credited to Kolbe, and widely quoted, is to the effect that a mixture of fumic nitric and fuming sulphuric acids is without action on methane even at 150° C.

Apparently there has been but one observed instance of the absorption of a gaseous paraffin by fuming sulphuric acid. Orndorff and Young[1] found that propane made from isopropyl iodide by the copper-zinc couple was slowly soluble in cold fuming sulphuric acid, the absorption amounting to over fifty per cent. in fifteen days, the acid taking a deep red color. In a former communication[2] I have shown that the higher members of the marsh-gas series are acted upon by fuming sulphuric acid, the products being true sulphonic acids. The peculiar fact brought out during this work that each hydrocarbon sulphonated at its boiling-point, suggested the idea that the gaseous members of the series would be soluble in cold fuming sulphuric acid, and this has been found to be the case.

METHANE.

1. *From Methyl Iodide.*—The methane employed in the first series of experiments was made from pure methyl iodide by the copper-zinc couple of Gladstone and Tribe.[3] The gas produced by the reaction was washed by passing through fuming sulphuric acid and was then allowed to stand over fuming sulphuric acid for three hours to free it of alcohol vapors. A portion was then measured off with the measuring burette and the absorption determined by passing it into the usual glass bead absorption pipette, filled with fresh fuming sulphuric acid.

In using this apparatus it is easy to so manipulate that after the gas has all been transferred to the absorption pipette, the bend in the capillary tube of the latter shall be filled with the acid, thus forming an effectual seal which prevents the gas from coming in contact with rubber connections. These rubber con-

[1] *Am. Chem. J.*, 15, 261
[2] *Am. Chem. J.*, 20, 664.
[3] *J. Chem. Soc.*, *1884*, 154.

nections were renewed frequently and the apparatus frequently tested for leaks with measured quantities of air. Two different absorption pipettes were used and any errors from leakage are highly improbable. The gas was each time run into a caustic potash pipette before a reading was made, in order to remove all acid vapors.

The data obtained in the first series are as follows:

Time between readings.	Observed volume. cc.	Loss. cc.	Loss. Per cent.
0	84.5	....	....
30 min	84.4	0.1	0.12
4 hours	79.0	5.4	6.39
2 "	77.3	1.7	2.01
12 "	74.0	3.3	3.90
24 "	67.2	6.8	8.04
5 days	56.2	11.0	13.01
1 day	54.0	2.2	2.60
2 days	49.9	4.1	4.85
1 day	46.1	3.8	4.48
11 days		38.4	45.40

The residue of 46.1 cc. was sealed into the pipette and allowed to stand over the fuming sulphuric acid during the three summer months. At the end of that time it had lost 22.2 cc., the residue amounting to only 23.9 cc. of the original 84.5 cc.—a total loss of 71.7 per cent. The color of the acid had changed from a light straw to a cherry-red and the absorption was still going on.

A comparison of the absorption figures in the above and in the following table shows apparent irregularities and discrepancies in the absorption at different periods for the same interval of time. This is easily accounted for by the variation in the barometer and thermometer on these different days, and for which variations no corrections were made when volumes were read, while the fact that the methane from methyl iodide shows a larger average daily absorption than that from natural gas is doubtless largely due to the much hotter weather prevailing during the former tests.

2. *From Natural Gas.*—The experiments with methane were repeated, using natural gas as the source of methane. The natural gas is piped to Lafayette from eastern Indiana, and analyzed as follows:

	Per cent.
Hydrogen sulphide and carbon dioxide	1.80
Oxygen	0.70
Heavy hydrocarbons	0.50
Carbon monoxide	0.60
Hydrogen	0.55
Nitrogen	3.80
Methane	92.05
	100.00

In a recent article by Prof. Phillips,[1] attention was called to the occurrence of hydrogen sulphide in a Canadian natural gas. This Indiana natural gas also contains large quantities of hydrogen sulphide, sufficient to give a pronounced odor to the gas and to rapidly precipitate a solution of lead acetate.

About 110 cc. of this natural gas were measured off and all constituents save nitrogen and methane removed by the ordinary method of gas analysis, using palladium sponge to remove hydrogen. The residue therefore consisted of ninety-six per cent. methane and four per cent. nitrogen.

The absorption was carried out as before described with the following results:

Time between readings.	Observed volume. cc.	Loss. Per cent.
0	100.00	....
16 hours	98.5	1.5
7 "	98.0	0.5
1 day	95.5	2.5
"	94.0	1.5
"	92.6	1.4
"	90.9	1.7
"	90.1	0.8
"	89.5	0.6
"	88.4	1.1
"	88.1	0.3
"	86.7	1.4
"	85.4	1.3
"	83.6	1.8
"	82.5	1.5
"	82.2	0.3
"	80.8	1.4
"	77.5	3.3
"	75.7	1.8
17 days		24.3

[1] This Journal, 20, 696.

That is, after remaining in contact with the fuming acid for seventeen days, a loss of 24.3 per cent. resulted,—an average daily absorption of one and four-tenths per cent. The residue was then sealed into the absorption pipette and allowed to stand three months during the winter. At the end of that time the total absorption amounted to 30.9 per cent.

ETHANE.

The ethane employed was made from pure ethyl iodide by the copper-zinc couple, washed by passing through fuming sulphuric acid, and was then allowed to stand for eighteen hours over fuming sulphuric acid to free it of all alcohol vapors. The absorption was carried out in the manner described for methane with the following results:

Time between readings.	Observed volume. cc.	Loss. cc.	Loss. Per cent.
0	95.0	....	....
1 day	91.3	3.7	3.89
"	84.7	6.6	6.95
"	79.5	5.2	5.47
"	75.8	3.7	3.89
"	70.2	5.6	5.89
"	65.0	5.2	5.47
"	61.1	3.9	4.10
"	57.3	3.8	4.00
"	53.2	4.1	4.32
"	48.2	5.0	5.26
"	43.0	5.2	5.47
"	39.5	3.5	3.68
"	36.2	3.3	3.47
"	32.0	4.2	4.42
"	28.0	4.0	4.21
15 days		67.0	70.5

In fifteen days, therefore, the absorption of ethane amounted to 70.5 per cent.,—an average daily absorption of 4.7 per cent. The residue was sealed into the pipette and allowed to remain in contact with the fuming acid for three months. At the end of that time the total absorption amounted to 88.3 per cent. As may be seen by comparison, the absorption of ethane is much more rapid than that of methane. Some oxidation results during this absorption, as carbon dioxide and sulphur dioxide are always produced. From the change in color of the acid it is probable that a sulphonic acid is also formed.

These results, establishing as they do the fact that methane and ethane are soluble in fuming sulphuric acid, are not without importance in their bearing toward gas analysis. A number of experiments were tried to determine the amount of absorption of each gas that took place in short intervals of time. After twenty-five per cent. of the methane obtained from natural gas had been absorbed, the residue was tested by measuring its absorption each hour. The results showed this absorption to be very slight, less than one-tenth cc. per hour. In the case of ethane, however, after over sixty per cent. had been absorbed, a similar series of experiments gave an average hourly absorption of 0.25 cc. equivalent to 0.60 per cent. of the ethane present.

In ordinary technical gas analysis, therefore, when the gas contains methane but no ethane, the absorption in the fuming sulphuric acid could be allowed to continue for an hour if necessary without much danger of serious error. But if ethane is present, fifteen minutes is the probable maximum of safety, and in any case the safest course to follow, especially in the case of an unknown gas, would be to shorten the time of contact with fuming sulphuric acid to the lowest possible limit.

LAFAYETTE, IND., October, 1898.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE VELOCITY OF THE REACTION BETWEEN SILVER ACETATE AND SODIUM FORMATE. A REACTION OF THE THIRD ORDER.[1]

BY ARTHUR A. NOYES AND GEORGE T. COTTLE.

Received October 28, 1898.

I. OBJECT OF THE INVESTIGATION.

THE investigations hitherto made of the velocities of those reactions in which two or more molecules of a substance enter have not yielded results of a general character. In many cases the velocity has been found proportional simply to the concentration of the substance, while in others it has been found proportional to that power of its concentration which corresponds to the number of its molecules entering into the reaction, as theoretical considerations would appear to demand. Thus, for ex-

[1] Read before the Boston meeting of the American Chemical Society, August 25, 1898.

ample, the reactions between iron salts and potassium chlorate,[1] between hydrogen peroxide and potassium iodide[2], and between potassium bromate and potassium iodide[2], in the presence of an excess of acid, are all simple reactions of the second order, although three or more molecules take part in the chemical change. In two cases, on the other hand, have the number of reacting molecules shown their influence; namely, that of the polymerization of cyanic acid,[3] and that of the reaction between stannous chloride and ferric chloride,[4] both of which, in correspondence with the number of reacting molecules, follow the law of the third order.

Further investigations of such reactions are therefore necessary. A new, and, it would seem, a suitable, example is the reaction between silver acetate and sodium formate, and we have, therefore, measured its velocity. The reaction is expressed by the following equation:

$$2AgC_2H_3O_2 + HCO_2Na = 2Ag + CO_2 + HC_2H_3O_2 + NaC_2H_3O_2$$

or, more correctly, according to the dissociation theory:

$$2\overset{+}{A}g + H\overset{-}{C}O_2 = 2Ag + CO_2 + \overset{-}{H}.$$

Thus it is a simple trimolecular reaction and should apparently follow the law of the third order, if any such reaction does so. We have selected a salt of formic acid in place of the acid itself and a silver salt of a very weak acid, in order to eliminate as far as possible the catalytic effect of the hydrogen ions.

II. DESCRIPTION OF THE EXPERIMENTS.

The sodium formate and the silver acetate used were prepared by recrystallizing the commercial salts, their purity being assured by qualitative tests. An exactly normal solution of the first, and a nineteenth normal of the second were made. The strength of the former solution was determined by addition of hydrochloric acid to a known amount in a platinum dish, evaporating to dryness, and weighing the residue; that of the latter by titration with potassium thiocyanate.

[1] Hood: *Phil. Mag.*, (5), 6, 371; 8, 121; 20, 323; Noyes and Wason: *Ztschr. phys. Chem.*, 22, 210.

[2] Noyes and Scott: *Ztschr. phys. Chem.*, 18, 118.

[3] Van't Hoff: Etudes de Dynamique Chimique, S. 90.

[4] Noyes: *Ztschr. phys. Chem.*, 16, 546.

As the velocity of the reaction is very small at ordinary temperatures, we carried on the experiments at 100°. For this purpose we constructed a steam thermostat out of a cylindrical tin can. In the cover, before it was soldered on, were cut one small hole, for a ball condenser, and five large holes, two inches in diameter, provided with quarter-inch tin collars covered with rubber tubing. In these were then placed large 225 cc. test-tubes containing the measured amounts of silver acetate solution and of water. In the cases where the concentration of the silver solution was 0.100 normal, solid silver acetate was weighed directly into the tube and the necessary amount of water added, as so strong a solution of the salt cannot be prepared in the cold. Each of the large tubes was then fitted with a cork through which were passed a small twenty-five cc. test-tube containing the required amount of formate solution and of water, a thermometer, an efficient glass stirrer, and tubes for blowing out samples. The water in the bottom of the thermostat was kept boiling constantly, and when the temperature of the solution had become quite constant, the bottom of the small tube was broken by a glass rod, the two solutions immediately mixed by violent stirring, and the time (to the second) noted. At definite moments samples of the mixture were blown out into measured amounts of ice-cold standardized potassium thiocyanate solution, thus instantly stopping the reaction. As the flasks containing the thiocyanate were weighed before and after addition of the sample, the amount of the latter was easily determined. The end-point was then determined after filtration by titration with silver nitrate and potassium thiocyanate solutions, using ferric alum as an indicator. Thus the silver content of the mixture and the progress of the reaction were ascertained.

III. EXPERIMENTAL RESULTS AND VELOCITY CONSTANTS.

The results of the experiments and the calculated velocity-constants are found in the following tables. All experiments were carried out at the temperature of water boiling under atmospheric pressure. A expresses the original concentration of the sodium formate, and B that of the acetate. Under t are found the time in minutes reckoned from the moment of mixing. Under $(B-x)_1$ and $(B-x)_2$ are given the concentrations of the silver

acetate found in two separate experiments after the time t, and under $B-x$ will be found the average of these results. Under C_2 and C_3 are given the constants of the second and of the third order respectively which occur in the equations:

$$\frac{dx}{dt} = C_2(A-x)(B-x) \text{ and}$$

$$\frac{dx}{dt} = C_3(A-x)(B-x)^2.$$

They are calculated, of course, from the corresponding integrated equations.[1] At the foot of each column of the C_2 values, is given the value, obtained by interpolation, corresponding to the time when the reaction is one-half completed. Under each column of C_3 values, the mean of the same is given.

FIRST SERIES.

$A = 0.100$; $B = 0.100$.

t.	$(B-x)_1$.	$(B-x)_2$.	$B-x$.	C_2.	C_3.
2	0.06694	.....	0.06694	2.57	30.8
4	0.05334	.....	0.05334	2.19	31.3
6	0.04684	.....	0.04684	1.89	29.6
9	0.03784	.....	0.03784	1.83	33.3
14	0.03235	.....	0.03235	1.61	30.6
				2.05	31.1

SECOND SERIES.

$A = 0.100$; $B = 0.050$.

2	0.03774	0.03776	0.03775	1.51	34.9
4	0.03090	0.03080	0.03085	1.35	35.1
7	0.02455	0.02425	0.02440	1.20	35.9
11	0.01959	0.01958	0.01959	1.04	35.6
17	0.01519	0.01483	0.01501	0.91	36.7
				1.22	35.6

THIRD SERIES.

$A = 0.050$; $B = 0.100$.

2	0.08112	0.08093	0.08103	2.67	29.9
4	0.07180	.....	0.07180	2.49	30.2
7	0.06395	.....	0.06395	2.36	31.2
11	0.05920	.....	0.05920	2.11	29.7
16	0.05625	.....	0.05625	1.88	28.0
				2.56	29.8

[1] Cf. Fuhrmann: *Ztschr. phys. Chem.*, 4, 89.

FOURTH SERIES.

$A = 0.050$; $B = 0.050$.

t.	$(B-x)_1$.	$(B-x)_2$.	$B-x$.	C_2.	C_3.
3	0.04019	0.04047	0.04033	1.60	35.8
8	0.03145	0.03173	0.03159	1.46	37.6
16	0.02473	0.02463	0.02468	1.28	38.8
25	0.02033	0.02066	0.02048	1.16	37.6
45	0.01629	.....	0.01629	0.92	37.4
80	0.01250	.....	0.01250	0.75	37.5
				1.29	37.4

FIFTH SERIES.

$A = 0.050$; $B = 0.0250$.

3	0.02192	.....	0.02192	0.91	38.7
5	.....	0.02004	0.02004	0.94	40.2
11	0.01634	.....	0.01634	0.85	43.0
12	.....	0.01579	0.01579	0.85	43.6
23	0.01194	0.01190	0.01192	0.76	45.8
				0.77	42.3

SIXTH SERIES.

$A = 0.0250$; $B = 0.050$.

10	0.03766	.....	0.03766	1.49	37.3
25	0.03136	.....	0.03136	1.44	38.6
45	0.02840	.....	0.02840	1.27	37.3
80	0.02653	.....	0.02653	1.08	34.4
				1.49	36.4

SEVENTH SERIES.

$A = 0.0250$; $B = 0.0250$.

10	0.02024	0.02009	0.02017	0.96	42.9
25	0.01626	0.01623	0.01624	0.86	43.8
45	0.01297	0.01276	0.01286	0.84	49.3
80	0.01140	0.01120	0.01130	0.61	39.0
				0.67	43.7

IV. DISCUSSION OF THE RESULTS.

Let us now consider the significance of the experimental results. In order to ascertain the order of a reaction and the influence of the individual substances upon its velocity, there are, as is well known, two different methods.[1] The first of these methods consists in determining the degree of the differential equation whose constants show the least variation during a sin-

[1] Cf. Noyes: *Ztschr. phys. Chem.*, 18, 119; 22, 215.

gle experimental series. A brief glance at the preceding tables suffices to show that, in every series, the values of C_2 exhibit a constant, and as a rule very considerable, diminution during the progress of the reaction. On the other hand, the tables also show that the values of C_3 remain practically constant. The reaction, judged by this method, is therefore one of the third order.

The second method of determining the order of a reaction consists in degree of the equation whose constants retain nearly the same value in *independent* series of experiments with very different original concentrations. This method is much more reliable than the former, because the effect of disturbances, such for example as the influence of the products of the reaction upon the velocity, in comparison with the much greater effect of the large variations in the original concentration, becomes of no consequence. In order to show more distinctly the results obtained by the application of this second method to the reaction considered here, we present the following table, in which the comparable values of the constants of both orders derived from the seven experimental series are given. Under C_3 the mean values are shown, while under C_2 the values are given which correspond to the state of the reaction in which one-half of the substance present in smallest amount has undergone change.

Series. No.	Normal concentration of Sodium formate.	Silver nitrate.	C_2.	C_3.
1	0.100	0.100	2.05	31.1
2	0.100	0.050	1.22	35.6
3	0.050	0.100	2.56	29.8
4	0.050	0.050	1.29	37.4
5	0.050	0.025	0 77	42.3
6	0.025	0.050	1.49	36.9
7	0.025	0.025	0.67	43.7

It is evident that the values of C_3 in all seven of the series are approximately the same, while those of C_2 vary about 280 per cent., which proves that the reaction is essentially one of the third order, and that its velocity is nearly proportional to the concentration of the sodium formate and to the square of the concentration of the silver acetate. In the case of this reaction, therefore, the two methods for the determination of the order of a reaction, lead to the same conclusion.

Still, we must not leave unmentioned the fact that the proportionality between the velocity and the square of the concentration of the silver acetate is not absolutely exact. While the change of the original concentration of the formate exerts no definite influence upon the constants of the third order, yet, as will be seen from the last table, there occurs with every diminution of the original concentration of the silver salt, a slight, but still unmistakable, increase in the values of the constants C_3. As to the cause of this phenomenon, nothing can be said with certainty. It is not improbable, however, that the greater velocity in the more dilute solutions depends upon the greater dissociation of the silver salt, it being then assumed that only the silver ions are capable of reacting.

V. SUMMARY.

By this research it is established that the reaction between sodium formate and silver acetate proceeds with a velocity which is proportional to the concentration of the former salt, and nearly proportional to the square of the concentration of the latter. As this reaction, according to prevailing molecular ideas, takes place between one molecule of the formate (or of its anion) and two molecules of silver acetate (or of its silver ion), its observed velocity is in accordance with the theoretical requirements, and it furnishes a new confirmation of the influence of the number of the molecules taking part in reactions.

COUMARIN AND VANILLIN, THEIR SEPARATION, ESTIMATION AND IDENTIFICATION IN COMMERCIAL FLAVORING EXTRACTS.[1]

BY WILLIAM H. HESS AND ALBERT B. PRESCOTT.

Received November 27, 1898.

IT is a common practice in preparing an extract of vanilla from vanilla beans, to introduce also, as a lower-priced material, a portion of tonka beans. This makes a cheaper article and one that is generally popular with consumers. It is understood, however, to be an inferior article when compared with the genuine, and it can no longer be correctly labeled "Vanilla Extract." Under this name the presence of tonka extract constitutes an adulteration and hence the separation, identification, and esti-

[1] Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

mation of coumarin, the odoriferous principle of the tonka bean, has become a practical problem for the analytical chemist.

THEORY FOR THE SEPARATION OF COUMARIN FROM VANILLIN.

Vanillin is hydroxymethoxybenzoic aldehyde, while coumarin is the anhydride of coumaric (orthohydroxycinnamic) acid. The separation depends on the aldehydic character of vanillin. If vanillin be dissolved in pure dry ether and dry ammonia gas passed through the solution, the aldehyde ammonia compound of vanillin will be precipitated in almost quantitative proportions. It is accordingly not very soluble in ether; but like all aldehyde ammonias it is very soluble in water. Ammonia water should, then, extract all the vanillin from an ether solution. This theoretic principle is fully borne out in practice, as has been proved by repeated experiment. Coumarin, on the other hand, remains wholly in the ether solution.

METHOD OF ANALYSIS.

A sample of 25 to 100 grams of the commercial extract to be examined is placed in an evaporating dish, and the alcohol is allowed to evaporate at about 80° C. Water is added from time to time to keep the amount of liquid about equal to the original volume. When the alcohol is all gone, normal lead acetate solution is added drop by drop until no more precipitate forms. Stirring with a glass rod aids in the flocculation and settling of the precipitate. The solution is now filtered, best through an asbestos funnel under pressure, and the precipitate washed with a few cubic centimeters of hot water. The cooled filtrate is now extracted with ether[1] by shaking out in a separatory funnel. About fifteen to twenty cc. of ether are used each time, and the process of shaking out is repeated until a few drops of the ether evaporated on a watch glass leaves no residue. If the shaking is done thoroughly, three to four times' shaking out will usually be sufficient to extract all the vanillin and coumarin. The combined ether extracts are introduced into a second separatory funnel and shaken out with dilute ammonia (one part strong ammonia to two parts of distilled water) using about two cc. of the alkaline water solution at a time, and repeating the

[1] Chloroform may be used instead of ether here and throughout the process, with this advantage that the evaporation of the chloroform leaves the residue dryer than it is when ether is used.

process until the ammoniacal solution is no longer colored yellow. The ether solution is washed with two cc. of water and this wash-water added to the alkaline extract. The ammoniacal solution is set aside for the estimation of vanillin. The ether solution is now poured out into an evaporating dish, and the ether allowed to evaporate spontaneously, or better, the dish containing the ether is placed in a vacuum desiccator over sulphuric acid, when the ether may be removed quickly. To prevent bumping of the ether and consequent loss during distillation *in vacuo*, a capillary tube sealed at one end is so placed in the liquid that the open end projects into the centre of the solution, while the sealed end extends well out of the liquid, and rests on the side of the dish. It is necessary that the tube be long enough to prevent its resting horizontally on the bottom of the dish.[1]

For Coumarin.—The residue having been left *in vacuo* over sulphuric acid long enough to remove all water, or else dried in an air-bath at not above 45° C., is treated with a few cubic centimeters of cold ligroin,[2] the latter being poured off into a clean dry weighed dish. The extraction with ligroin is repeated until a drop evaporated on a watch-glass leaves no residue. The ligroin is allowed to evaporate (best *in vacuo* in a desiccator containing paraffin), is dried at not above 45° C. and weighed. This gives pure crystalline coumarin, melting at 67° C. After weighing, a melting-point determination should be taken, and this, with the odor which is characteristic at this point in the analysis when compared with that of a known sample, is sufficient for its identification.

For Vanillin.—The ammoniacal solution obtained above is rendered slightly acid with ten per cent. hydrochloric acid. It is then shaken out with ether in the manner stated before. The ether is removed and the residue is dried *in vacuo* over sulphuric acid or else in an air-bath at not above 55° C. This residue is washed repeatedly with boiling ligroin, using a few cubic centimeters at a time to remove the vanillin and free it from adhering substances. The ligroin solution is decanted into a weighed

[1] Tiny capillary tubes are very useful in preventing bumping in boiling liquids, and are made by drawing out a glass tube to the dimensions of a hair. Cut the tube into a convenient length and fuse up one end.

[2] A petroleum fraction boiling between 30° and 40° C.

dish, the ligroin is removed, the vanillin is dried at not above 55° C. and weighed. This gives a pure crystalline product, melting at 80°–81° C. After the weighing, a melting-point determination should be made, and then color tests may be applied. Some samples of vanilla extracts have been found to contain phenol-like bodies resembling creosol in odor and chemical behavior. These give color compounds with salts of iron; hence, any volumetric estimation, or even qualitative test, applied to the unpurified extract may be fallacious when based on color reactions of iron salts.

Results were obtained by this method under control as follows: From Mexican vanilla beans, a liquid product was made by following the directions of the United States Pharmacopoeia. Of this tincture, twenty-five grams were taken in duplicate portions; to each was added five-tenths gram of pure crystallized coumarin, and the analysis was made for estimation of coumarin and of vanillin. The coumarin recovered from the duplicate portions was, respectively, 0.491 gram or 98.2 per cent. of that taken, and 0.482 gram or 96.4 per cent. of that taken. The vanillin recovered was, respectively, 0.3081 gram and 0.2997 gram, from each of the portions of twenty-five grams of the tincture.

This method for vanillin is much easier and quicker to work than the sodium bisulphite method, and has these advantages: (1) the shaking out with ammonia water is quickly done; (2) the alkaline solution of vanillin thus obtained is small in bulk; (3) the trouble of getting rid of sulphur dioxide is avoided. The separation of the vanillin is also more complete.

UNIVERSITY OF MICHIGAN,
November 18, 1898.

NEW METHOD FOR THE PREPARATION OF CESIUM.[1]

BY HUGO ERDMANN AND A. E. MENKE.

Received October 19, 1898.

WINKLER[2] tried to reduce cesium carbonate with metallic magnesium, in both glass and porcelain tubes in a current of hydrogen. He, however, obtained no cesium. Beketoff[3] states that it can be obtained in small quantities by the electrolytic reduction of the cyanide; he also acted on the hydrate with aluminum, but the yield was poor. In 1894 he

[1] Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

[2] *Ber. d. chem. Ges.*, **23**, 53.

[3] *Bull. Acad. Petersburg*, **4**, 247.

made a small amount by acting on cesium alum with metallic magnesium.[1] We made a great many experiments with a view to improving these processes, but finally found that a different method worked remarkably well, and if the directions are exactly followed it is absolutely free from danger. We found that by heating cesium hydroxide with magnesium powder in a red-hot tube through which passed a current of hydrogen, we could obtain nearly the theoretical amount of cesium. Inasmuch as we always commenced with cesium alum, and as that is the cheapest and most available salt to begin with, we will give all the details of the method that we finally found to be the best. The cesium alum should be first converted into cesium sulphate. It is not advisable to convert it directly into cesium hydroxide on account of the fact that too much water is required to dissolve the cesium alum, and also because cesium hydroxide absorbs carbon dioxide very rapidly. In order to convert cesium alum into cesium sulphate the following reaction can be used:

$$2CsAl(SO_4)_2.12H_2O + 3Ba(OH)_2.8H_2O = Cs_2SO_4 + 2Al(OH)_3 + 3BaSO_4 + 48H_2O.$$

Dissolve the cesium alum in as small a quantity of boiling-water as possible (it is more convenient in all operations connected with cesium to use casseroles rather than dishes or beakers), and in a separate casserole dissolve the crystalline barium hydroxide; when both are in solution, mix the two and filter rapidly with a good pump; a Buchner funnel can be used in this operation to great advantage. The filtrate if slightly alkaline, due to an excess of barium hydroxide, should be treated with carbon dioxide for a few minutes and quickly refiltered. It can now be either evaporated to dryness or crystallized. The next step is to convert the cesium sulphate into cesium hydroxide.

$$Cs_2SO_4 + Ba(OH)_2.8H_2O = 2CsOH + BaSO_4 + 8H_2O.$$

The sulphate is quite soluble in hot water, and as small a quantity of the solvent as possible should be used. The barium hydroxide should also be separately dissolved in a very small quantity of water. When both are in solution mix and filter with a suction-pump and Buchner funnel. The filtrate is

[1] *Proc. Russ. Phys. Chem. Ges.*, 1894.

rapidly evaporated to dryness in a silver crucible and then fused; it should now be poured into a silver dish so that it will make a thin brittle cake of cesium hydroxide, which must not be exposed to the air longer than is absolutely necessary; it is quickly broken, transferred to a warm dry bottle, and weighed; then put into a hot porcelain mortar, broken into small pieces about half the size of a pea, and mixed with one-half its weight of magnesium powder (the magnesium powder must be previously heated in a current of hydrogen to get rid of the fat with which it is always mixed); the mixture is then quickly dropped into a clean, dry, rust-free malleable iron tube of the following dimensions: one meter long, fifteen mm. diameter, three mm. thick, and fifteen cm. from the end it is bent to an angle of about 125°. In order to keep the mixture in the tube a small bundle of clean piano wire irregularly twisted together is forced into the tube down the long part to the angle, before dropping in the mixture. In filling the tube it is best held inclined. The tube is now laid in a slightly inclined combustion furnace, to aid the flow of the liquid metal and quickly connected to a Kipp hydrogen generator. The hydrogen must be passed through permanganate solution in order to oxidize hydrogen arsenide and then thoroughly dried by sulphuric acid and phosphoric anhydride; the bent end of the tube is immersed in liquid paraffin to the depth of about two cm. It is advisable to have the paraffin in a casserole about seven and one-half cm. in diameter. To begin the distillation, light the burner farthest away from the mixture (the tube should never be more than one-third full), and allow hydrogen to pass through at the rate of about forty bubbles per minute. When the temperature has risen as high as one burner can produce, light the next but do not turn on full pressure immediately; this process must be continued, burner by burner, until reaction begins. This is readily marked by an increase in the speed of bubbling through the paraffin. If the bubbles come faster than 80–100 per minute, turn out the last-lighted burner and remove the tile over the tube. Bubbling will now gradually cease, due to the probable formation of hydride of cesium, decomposed at high temperatures; consequently the hydrogen pressure must be increased until gas comes through the paraffin. When

the back suction is relieved the hydrogen stream can be restored to its normal rate. This operation must be continued until all the burners are lighted and the temperature is full red. The angle piece of the tube, which should be as close to the furnace as possible, is now heated by a powerful Bunsen burner, and constantly struck with a piece of iron. The metallic cesium which has distilled into this part of the apparatus, will be liquefied, and will trickle down under the paraffin, collecting in silvery drops. The cesium comes out of the tube at the very end of the process and not before. If the foregoing directions are closely followed the whole operation can be accomplished in four hours without the slightest difficulty or danger. Explosions only occur when the tube is heated too rapidly and not sufficient attention paid to the pressure regulation. It is evident from the result of these experiments that Winkler was mistaken in stating that it is impossible to obtain cesium from its compounds by the aid of magnesium. We made cesium in quantity by our method and are now studying its physical properties.

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THE OXIDATION OF FORMIC ALDEHYDE BY HYDROGEN PEROXIDE.[1]

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A FEW preliminary experiments seemed to indicate that the oxidation of formic aldehyde by hydrogen peroxide, could be easily and certainly followed by determining the quantities of formic acid produced as the result of the oxidation, by standard alkali, using phenolphthalein as the indicator. A study of this oxidation was therefore undertaken. A number of oxidations, involving hydrogen peroxide as the oxidizing agent, have been studied. The work of Magnanini[2] and that of Harcourt[3] and Essen on the effect of this substance on hydriodic acid, under different physical and chemical conditions, is important and interesting in this connection. A study of the oxidation of gaseous acetic aldehyde by oxygen gas was undertaken a short

[1] Read before the Boston meeting of the American Association for the Advancement of Science, August 25, 1898.

[2] *Gaz. chim. ital.*, **20**, 377, *1890*.

[3] *Phil. Trans.*, *1867*, **157**, 20, 460 and *Phil. Trans.*, *1895*, **186**, 817, 895.

time ago by van't Hoff[1] with the view of determining the relation of the pressure under which the oxygen acts to the rate of oxidation. He found the oxidation to proceed with convenient speed at 20° C. and observed that the action was affected by light. His results showed the velocity of the oxidation to be proportional to the pressure of the aldehyde vapor, and to the square root of the pressure of the oxygen. So far as we have been able to discover, this is the only case of the kind that has ever been investigated. It seemed to us, therefore, all the more important to undertake the study of the oxidation of formic aldehyde by hydrogen peroxide in aqueous solution. Marchand's hydrogen peroxide and Schering's formaldehyde were used in the investigation. The solution of formaldehyde was standardized by heating with potassium hydroxide, and the hydrogen peroxide by means of a standard solution of potassium permanganate. The peroxide was always standardized immediately before using, in order to correct any change in strength that it might have undergone. Normal solutions of formaldehyde and peroxide were employed in equivalent volumes, so that in all cases, not stated to the contrary, the reaction was studied at half-normal dilution.

The effect of temperature was first investigated. Our preliminary experiments indicated that the reaction proceeded with extreme slowness at ordinary temperatures, but with great velocity at the temperature of boiling water. It was therefore decided to conduct a series of experiments at each of the following temperatures; *viz.*, 20° C., 26° C., 40° C., 50° C., 60° C., 70° C., 80° C., 90° C., and 98° C. It should be said further that these several series were tried in dark, it having been observed that light exerted an accelerating influence on the progress of the reaction. In each of these experiments five cc. of normal formaldehyde was placed in a test-tube, together with five cc. of normal hydrogen peroxide; the tube was then sealed and placed in a water-bath, which was maintained constant at the temperature desired. The tube was then exposed to certain temperatures for different intervals of time, at the end of which they were plunged into cold water, opened and their contents titrated with fifth-normal potassium hydroxide. The coefficients of

[1] Etudes de Dynamique Chimique, *1895*, p. 79.

velocity were then calculated from the results by the equation for bimolecular reactions:

$$\frac{1}{\theta}\left(\frac{x}{A-x}\right)\frac{1}{A} = K$$

where θ represents time in minutes, A the initial amount of the substance present, x the amount of substances changed, and K is the constant which measures the velocity of the reaction.

The following are the tabulated results of the series together with the calculated coefficients of velocity:

SERIES AT 40°.

Time. Minutes.	Fifth-normal potassium hydroxide neutralized. cc.	Decomposed. Per cent.	Coefficient of velocity.
30	0.29	1.16	0.0000157
60	0.63	2.52	0.0000172
90	0.97	3.88	0.0000179
120	1.32	5.28	0.0000185
150	1.71	6.84	0.0000196
180	2.00	8.00	0.0000193
222½	2.48	9.92	0.0000198
240	2.65	10.60	0.0000198
270	3.10	12.40	0.0000208
300	3.47	13.88	0.0000201
		Average coefficient of velocity,	0.0000189

SERIES AT 50°.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
30	1.10	4.40	0.0000614
60	2.13	8.52	0.0000621
90	3.30	13.20	0.0000676
120	4.45	17.80	0.0000722
150	5.20	20.80	0.0000700
180	5.85	23.40	0.0000679
210	6.90	27.60	0.0000726
240	7.63	30.52	0.0000732
270	8.10	32.40	0.0000710
300	9.00	36.00	0.0000750
		Average coefficient of velocity,	0.0000693

SERIES AT 60°.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
75	7.75	31.00	0.000240
90	8.95	35.80	0.000248
105	9.75	39.00	0.000244
120	10.75	43.00	0.000251
135	11.45	45.80	0.000250
150	11.90	46.70	0.000244
165	12.55	50.20	0.000244
180	13.20	52.80	0.000249
195	14.15	56.60	0.000268
210	14.35	57.40	0.000257
225	14.70	58.80	0.000254
240	15.00	60.00	0.000250
255	15.5	62.00	0.000256
270	15.90	63.60	0.000259
285	16.15	64.60	0.000255
300	16.23	64.92	0.000247
		Average coefficient of velocity,	0.000251

SERIES AT 70°.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
15	5.15	20.60	0.000691
45	11.25	45.00	0.000727
60	13.20	52.80	0.000746
75	14.80	59.20	0.000774
90	15.65	62.60	0.000744
105	16.65	66.60	0.000760
120	17.45	69.80	0.000770
135	17.65	70.60	0.000711
150	17.75	71.00	0.000653
165	19.20	76.80	0.000802
180	19.55	78.20	0.000799
195	19.95	79.80	0.000772
210	20.65	82.60	0.000754
225	20.65	82.60	0.000704
240	20.65	82.60	0.000660
		Average coefficient of velocity,	0.000711

SERIES AT 80°.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
10	10.15	40.60	0.00273
20	13.85	59.40	0.00248
35	16.93	67.72	0.00240
50	19.05	76.20	0.00256
60	19.85	79.40	0.00257
80	20.60	82.40	0.00234
100	21.60	86.40	0.00254
120	21.95	87.80	0.00240
150	22.80	91.20	0.00276
		Average coefficient of velocity,	0.00253

SERIES AT 90°.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
5	12.10	48.40	0.00750
15	17.20	68.80	0.00590
20	18.54	74.16	0.00555
30	20.60	82.40	0.00625
50	21.70	86.80	0.00525
60	22.80	91.20	0.00690
		Average coefficient of velocity,	0.00625

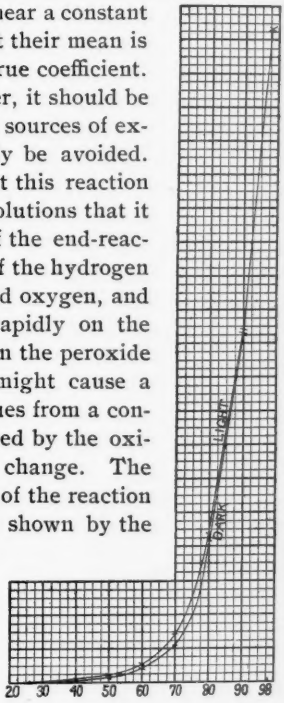
It was noted that considerable pressure was developed in the tubes up to this temperature, *viz.*, 90° C., owing to the fact that the hydrogen peroxide liberates its oxygen more rapidly than it is capable of acting on the formaldehyde; but at this temperature the pressure almost disappears indicating that the peroxide acts on the formic aldehyde at this temperature very nearly as rapidly as it is capable of liberating its oxygen.

SERIES AT 98°.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
10	18.90	75.60	0.0124
15	20.50	82.00	0.0122
20	21.60	86.40	0.0127
30	22.30	89.20	0.0110
45	23.06	92.24	0.0106
60	23.50	94.00	0.0105
		Average coefficient of velocity,	0.0116

A few experiments were tried at lower temperatures; at 20° the coefficient of velocity was found to be approximately 0.000000855, and at 26°, 0.00000199.

In harmony with the theory of bimolecular reactions the coefficients of velocity of this reaction, for any particular temperature, approach a constant value. This is especially true of the values obtained for 50° C., 60° C., and 70° C., and in all cases they are probably sufficiently near a constant value to justify one in assuming that their mean is a very close approximation to the true coefficient. In considering these results, however, it should be borne in mind that there are several sources of experimental error which can scarcely be avoided. One of these is due to the fact that this reaction takes place so rapidly in alkaline solutions that it is difficult oftentimes to make sure of the end-reaction. Then, again, a small amount of the hydrogen peroxide decomposes into water and oxygen, and this liberated oxygen acts far less rapidly on the formaldehyde than that contained in the peroxide molecule. A third factor which might cause a slight departure of the observed values from a constant is that the formic acid produced by the oxidation very slightly accelerates the change. The effect of temperature on the course of the reaction under consideration is very clearly shown by the curve. On this, temperatures have been laid off on the axis of abscissas, the ordinates being the average coefficients of velocity of the reaction, multiplied, for convenience, by $3333\frac{1}{3}$. The enormous but regular effect of temperature on the velocity of this reaction is clearly shown by this curve. From 20° to 40° C. it will be observed that the curve is nearly coincident with the axis of x; then, very slowly at first, but very rapidly later on, it begins to diverge from it, until at 90° to 98° C. it is almost perpendicular to it, indicating that we would not have to raise the temperature



Ordinates = Average Coefficients of velocity × $3333\frac{1}{3}$.

of the system any very great deal in order to make the change practically instantaneous.

The effect of light on the progress of reaction has also been investigated. The fact that hydrogen peroxide is more unstable in the light than in the dark would naturally lead to the supposition that light would probably accelerate the oxidation under discussion. A few preliminary experiments indicated that such was really the case. Two tubes, each containing ten cc. normal formic aldehyde and ten cc. normal hydrogen peroxide, were kept at 20° C., one in the sunlight and one in the dark, for five and one-half hours. The tube in the dark showed a decomposition of seven-tenths per cent., whereas that in the light gave four per cent. decomposition. It was therefore decided to carry through several series in the direct sunlight at the same temperature as those which were tried in the dark, and under conditions as nearly identical as possible. The extremely variable character of even bright sunlight is capable of causing variations in the velocity of the reaction in the same series, so that for the several series in the sunlight the values of K show greater deviation from a constant value than those obtained for the same series in the dark. In light at 20° the coefficient of velocity was found to be 0.00000505 and at 26°, 0.00000629.

SERIES IN DIRECT SUNLIGHT AT 40° C.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
45	0.75	3.00	0.0000275
60	1.00	4.00	0.0000278
90	1.85	7.40	0.0000355
120	2.85	11.40	0.0000429
150	3.30	13.20	0.0000401
180	4.40	17.60	0.0000475
240	5.10	20.40	0.0000427

Average coefficient of velocity 0.0000378, thus showing an increase of 100 per cent. over the average coefficient of velocity in the dark at the same temperature.

SERIES IN DIRECT SUNLIGHT AT 50° C.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
60	3.35	13.40	0.000104
75	4.05	16.20	0.000103
90	4.85	19.40	0.000107
105	5.45	21.80	0.000106
120	6.95	27.80	0.000128
135	7.15	28.60	0.000119
150	7.70	30.80	0.000119
165	8.65	34.60	0.000128
180	10.35	41.40	0.000156
195	11.05	44.20	0.000162
215	11.78	47.12	0.000168
233	11.78	47.12	0.000153
		Average coefficient of velocity,	0.000129

SERIES IN DIRECT SUNLIGHT AT 60° C.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
30	3.85	15.40	0.000243
45	5.30	21.20	0.000239
60	6.65	26.60	0.000242
75	8.05	32.20	0.000253
90	8.85	39.40	0.000288
105	10.75	43.00	0.000287
120	11.53	46.12	0.000285
135	12.35	49.40	0.000290
150	13.39	53.56	0.000308
165	13.63	54.52	0.000291
180	15.01	60.04	0.000336
195	15.85	63.40	0.000356
216	16.35	65.40	0.000350
225	16.40	65.60	0.000339
270	18.20	72.80	0.000397
300	19.05	76.20	0.000427
		Average coefficient of velocity,	0.000308

SERIES IN DIRECT SUNLIGHT AT 70° C.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
45	5.95	47.60	0.000805
90	7.95	63.60	0.000777
135	9.45	75.60	0.000918
180	10.15	81.20	0.000959
		Average coefficient of velocity,	0.000865

SERIES IN DIRECT SUNLIGHT AT 80° C.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
20	13.85	55.40	0.00248
35	17.10	68.40	0.00247
50	18.90	75.60	0.00248
60	20.00	80.00	0.00267
80	21.31	85.20	0.00288
100	21.95	87.80	0.00288
120	21.95	87.80	0.00240
150	23.00	92.00	0.00307
225	23.20	92.80	0.00228
		Average coefficient of velocity,	0.00262

SERIES IN DIRECT SUNLIGHT AT 90° C.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
15	17.30	69.20	0.00595
20	19.30	77.20	0.00675
30	20.40	81.60	0.00590
55	22.10	88.40	0.00555
75	23.20	92.80	0.00690
		Average coefficient of velocity,	0.00621

The results, like those obtained in the dark, can best be represented graphically by the curve, the abscissas of which represent the temperatures and the ordinates the average coefficients of velocity multiplied by $3333\frac{1}{3}$. From this it will be seen, at a glance that for certain temperatures, at least, light exerts an accelerating influence on the progress of the reaction. The point of chief interest, however, is that the effect of light is different for different temperatures. What it is at 0° C. we have not yet had an opportunity to determine, in consequence of the extreme slowness of the change. Generally, however, it will be seen that the accelerating effect of light is greatest for low temperatures, gradually diminishing with increasing temperature until at a temperature just a little below 90° C., the curves intersect and become identical for light and dark. When we compare the velocity of this reaction at 20° C. and 40° C. and observe the great falling off in the rate of change it can be fairly surmised that somewhere, probably not very far removed from 0° C. on either side, the reaction would cease altogether, both in light

and dark. It would seem then that the accelerating influence of light is possible only between certain rather narrow limits of temperature. That such is the case seems to have been proved also, for reactions other than the one under discussion. Amato[1] has shown, for example, that if a mixture of hydrogen and chlorine be cooled to —12° C. it could be exposed to direct sunlight for hours without any combination taking place. It is further conceivable with reference to this particular reaction that at very high temperatures it would take place so rapidly that light would be without effect on the change. In the same way Beatty[2] and one of us have shown that while light cannot cause the combination of hydrogen and bromine at ordinary temperatures, it greatly accelerates their combination at 197° C.; at still higher temperatures it is quite possible that its effect on this system would be lost. The chemical action of light is at best so little understood that considerable interest attaches to these results which would seem to support the view that a certain amount of the energy of the light actually enters into, and becomes a part of, the system undergoing change. Below a certain temperature the heat and light energy together might be insufficient to cause the change. At temperatures at which the given reaction becomes possible, however, light would accelerate, for the reason that the increment of energy furnished by it would be a measurable amount of the entire quantity of energy present. At very high temperatures this increment of light energy would become so small, as compared with the increased heat energy of the system, as to cause the effect of the light to disappear altogether.

ON THE EFFECT OF ACIDS AND BASES ON THE OXIDATION.

It has been announced as a general proposition that "all oxidation and reduction processes are accelerated by the presence of free acids, in proportion to their coefficients of affinity."[3] It was therefore deemed desirable to try the effect of acids on this particular case. In order to do this, three series of experiments were carried through at 50° C.: one with hydrochloric

[1] *Gazz. chim. ital.*, **14**, 57.
[2] *Am. Chem. J.*, **20**, 159.
[3] Schlundt and Warder: *Am. Chem. J.*, **18**, p. 31.

acid, one with formic acid, and one with water alone. In each experiment five cc. normal formaldehyde, five cc. normal hydrogen peroxide, and five cc. of water or the acid were mixed, placed in sealed tubes and kept at 50° C. for the several desired intervals of time. The following series were carried through:

(1) With hydrochloric acid 0.0000754
(2) With formic acid 0.0000705
(3) With water 0.0000670

HYDROCHLORIC ACID SERIES.

Mixture: Five cc. normal hydrogen peroxide, five cc. normal formaldehyde, and five cc. normal hydrochloric acid.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
60	2.25	9.00	0.0000659
90	3.53	14.12	0.0000737
120	4.33	17.32	0.0000698
180	6.55	26.20	0.0000789
210	7.45	29.80	0.0000809
240	8.00	32.00	0.0000784
270	8.75	35.00	0.0000799
		Average coefficient of velocity,	0.0000754

FORMIC ACID SERIES.

Mixture: Five cc. normal hydrogen peroxide, five cc. normal formaldehyde, and five cc. normal formic acid.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
60	2.10	8.40	0.0000611
90	3.15	12.60	0.0000641
120	4.40	17.60	0.0000745
150	5.08	20.32	0.0000680
180	6.20	24.80	0.0000733
210	6.95	27.80	0.0000733
240	7.80	31.20	0.0000756
270	8.40	33.60	0.0000750
		Average coefficient of velocity,	0.0000705

SERIES WITH WATER.

Mixture: Five cc. normal hydrogen peroxide, five cc. normal formaldehyde, and five cc. water.

Time. Minutes.	Fifth-normal potassium hydroxide. cc.	Decomposed. Per cent.	K.
60	2.10	8.4	0.0000611
90	3.20	12.8	0.0000652
120	4.07	16.28	0.0000648
150	4.90	19.60	0.0000650
180	5.88	23.52	0.0000680
210	6.92	27.68	0.0000730
240	7.30	29.20	0.0000690
270	8.12	32.48	0.0000712
		Average coefficient of velocity,	0.0000670

It will be observed that the acids caused some acceleration in the rate of change, and that hydrochloric acid caused a greater acceleration than formic. It is not by any means so marked as it is in certain other oxidations that have been studied, a fact that can doubtless best be explained by assuming that the accelerative tendency of the acid is counterbalanced to some extent by an increased stability in the hydrogen peroxide, which latter is also brought about in some way by the acid. The acceleration produced by formic acid, however, is probably sufficiently great to account for the increase in velocity usually observed at the end of a long series. The formic acid produced during the oxidation would cause the reaction to proceed more rapidly towards the end. The effect of bases on the rapidity of the oxidation is certainly most remarkable. In consequence of the rapidity of the oxidation, all of our experiments with bases have been conducted at ordinary temperatures. In each experiment five cc. normal formaldehyde and five cc. normal hydrogen peroxide were placed in a flask, and a quantity of half-normal base then added—equivalent to the amount of formic acid produced by the oxidation, and from the time of adding the solution of the base the duration of the experiment was counted. At the end of a given time an amount of normal hydrochloric acid was added—equivalent to the original amount of base present—and the solution was then titrated back with standard caustic potash, using phenolphthalein as an indicator. During the progress of the reaction with bases, considerable effervescence occurred, due to escaping oxygen. The reaction is affected by

light, and slight changes in temperatures also produced quite a noticeable effect on the rate of change.

Caustic potash, caustic soda, and ammonia were first compared as to their effect on the reaction, each active substance reacting in fourth-normal solution. The results obtained are given in the following table.

TABLE I.

Time. Minutes.	Potassium hydroxide. Per cent.	Sodium hydroxide. Per cent.	Ammonium hydroxide. Per cent.
2	48.4	46.0	15.0
4	62.5	61.0	24.0
6	70.0	69.0	31.0
8	76.5	74.0	37.0
10	78.0	77.0	40.0
15	87.0	88.0	44.0
20	99.5	99.0	49.0
25	....	....	54.4
35	....	....	56.0
83	....	....	69.0
1350	....	....	86.4

These results are of interest, first, as showing the remarkable acceleration produced by alkalies on the progress of this reaction. Few, if any, attempts have been made to follow any reaction occurring with such rapidity. It will be seen, further, that caustic potash and soda are practically the same in their effect, and that both act much more vigorously than ammonia. This is in harmony with our present knowledge respecting the activity of these bases. The action of barium hydroxide on this oxidation was also tried. Owing to lack of solubility, it could not be compared with these bases at the dilution at which the above comparisons were made. As concentrated a solution as possible of this base was made (which happened to be nearly third-normal), 14.5 cc. being equivalent to five cc. normal hydrochloric acid. This was compared with caustic potash of exactly the same strength, so that in these experiments the active substances were present in about fifth-normal solution. In each experiment five cc. normal formic aldehyde, five cc. hydrogen peroxide, and 14.5 cc. of the given base were employed. The following results were obtained:

TABLE II.

Time. Minutes.	Potassium hydroxide. Per cent.	Barium hydroxide. Per cent.
2	43.0	53.4
4	57.0	67.4
6	63.0	68.0
8	66.4	71.0
10	72.0	74.0
15	74.4	78.0
20	82.4	81.0
25	84.4	82.4
30	85.0	86.0

In the last five experiments of this series it will be observed that caustic potash and barium hydroxide are exerting practically the same effect on the rate of oxidation. At first, however, the barium hydroxide acts more rapidly. In the experiments with barium hydroxide at this dilution we always obtained a white precipitate, probably barium dioxide, and this may have altered the conditions to such an extent as to cause this difference in the effect of these two bases. It is our intention to study the effect of bases at greater dilutions, so as to include lime and strontium hydroxide in the comparison. The great acceleration produced by bases on this oxidation has suggested another important line of work, in which only the merest beginning has as yet been made. This is with reference to the hydrolysis of salts. It was thought that this reaction might furnish us with a very delicate method for the measurement of the hydrolysis of alkaline salts. It has been found, for example, that while common salt is without influence on rate of change at 50° C., it is greatly accelerated by sodium acetate. We have not yet had an opportunity to make any thorough study of this phase of the reaction, but the following comparisons of the action of hundredth-normal potassium hydroxide and normal sodium acetate is interesting, as showing the possibilities of this method in measuring the hydrolysis of salts.

Two series of experiments were tried, in the dark, at 60° C. In series No. 1, one cc. normal formaldehyde was mixed with one cc. normal hydrogen peroxide, one cc. hundredth-normal caustic potash, and seven cc. of water in each experiment. In series No. 2, exactly the same quantities of substances were used, except that instead of hundredth-normal caustic potash, one

cc. normal sodium acetate was employed. The coefficients of velocity obtained in the two series are given in Table III.

TABLE III.

Time. Minutes.	Series No. 1, potassium hydroxide.	Series No. 2, normal sodium acetate.
68	0.000141	0.000218
90	0.000141	0.000209
120	0.000156	0.000231
Average	0.000146	0.000219

These results would indicate that at this temperature and dilution, sodium acetate is hydrolyzed to the extent of over one per cent. This number is probably not far from the truth. A more thorough study especially of this last phase of the reaction will soon be undertaken.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, July, 1898.

UPON THE ACTION OF SULPHURIC ACID ON THYMOL.[1]

[THIRD PAPER.]

BY JAMES H. STEBBINS.

Received December 15, 1898.

MY motive in taking up this subject again, is for the purpose of clearing up certain doubts which had arisen in my mind, in connection with my previous experiments.[2]

Photomicrographic examinations of the products previously obtained showed so many different forms of crystallization, that I was led to believe that by the treatment of thymol with 66° sulphuric acid, at steam-bath temperature, possibly several isomeric acids are formed.

To gain more light upon this question, therefore the following experiments were made :

Sixty grams of powdered thymol were heated in a beaker on the water-bath, under constant stirring, with fifty grams of 66° sulphuric acid, until the mixture solidified to a crystalline mass, which occurs after nine to ten minutes' heating.

As previously noted, a small quantity of a clear, oily-looking liquid separates, on pressing, from the crystalline cake. This, on being poured off into a beaker, solidifies on cooling to a mass of minute white needles.

[1] Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

[2] This Journal, **3**, 103, 110, (*1881*).

This product was marked "A" and set aside for further examination.

The main crystalline mass or product "B", resulting from the action of sulphuric acid on thymol, was dissolved in hot water and filtered from a small quantity of a dark oily-looking liquid which floated on its surface and which appeared to be thymol. The filtrate was then neutralized with barium carbonate, filtered from the barium sulphate, and concentrated on the water-bath, till crystals began to show on the surface of the liquid. It was then set aside to crystallize.

A large crop of white flat-sided prisms was obtained. These were sucked as free from mother-liquid as possible, by the aid of a suction-pump and, after pressing between folds of filter-paper, were redissolved in a small quantity of hot water and the solution set aside to crystallize.

A barium salt "B" is thus obtained, which contains water of crystallization, a part of which is lost on exposure to the air, or over sulphuric acid, and the whole of it is driven off under partial decomposition of the salt, when the latter is heated to 100°.

One of the peculiarities of this salt, is the fact that it crystallizes from water in several crystalline forms, according as to whether the crystallization is allowed to take place gradually or rapidly.

By the slow evaporation of its aqueous solution, it is obtained in the shape of rhombic plates or prisms (Figs. 1 and 2). By a more rapid evaporation of the aqueous solution, it may be obtained in striated crystals, radiating from a common center (Fig. 3).

0.9324 gram substance, dried at 100°, lost 0.0724 gram water, equal to 2.55 molecules,—or in round numbers $2\frac{1}{2}$ molecules of water of crystallization.

0.760 gram substance, dried at 100°, gave 0.2961 gram barium sulphate.

	Theory for $\left((C_6H_3)(CH_3)(C_3H_7)\langle^{OH}_{SO_3}\right)_2 Ba$.	Found.
Ba	23.02	22.90
$2\frac{1}{2}$ H_2O	7.03	7.84

Therefore the barium salt of what I will temporarily call

alphathymolsulphonic acid has the following empyrical formula:

$$\left((C_6H_2)(CH_3)(C_3H_7)\begin{matrix}OH\\SO_3\end{matrix}\right)_2 Ba + 2\tfrac{1}{2}\ H_2O.$$

A comparison of my product with the barium salt of the alphathymolsulphonic acid, described by Engelhardt and Latschinoff,[1] shows that they are identical in all respects, save the water of crystallization. Engelhardt and Latschinoff claim two molecules of water of crystallization for their barium salt, while I find that mine crystallizes with two and one-half molecules of water of crystallization.

The barium salt of alphathymolsulphonic acid, above described, is very easily soluble in water and alcohol, from which, as already stated, it crystallizes in various forms, dependent upon the manner in which crystallization is brought about.

FREE ALPHATHYMOLSULPHONIC ACID.

In one of my previous papers[2] a method was described for obtaining this compound from its lead salt, by precipitating the lead with hydrogen sulphide. It may, however, also be prepared from its barium salt, by treating the latter with sufficient sulphuric acid to precipitate out all the barium present as barium sulphate. The latter is then collected upon a filter, washed, and the filtrate concentrated to the consistency of a sirup on the water-bath. On standing, the free thymolsulphonic acid crystallizes out, in the shape of rhombic plates or tables (Fig. 4). If, however, the sirup be agitated, or better still, if the bottom of the crystallizing dish be scratched with a glass rod, the sulphonic acid will be obtained in the shape of rhombic prisms grouped together fern-shaped and may at times be accompanied by some rhombic plates (Fig. 5). It is freely soluble in both hot and cold water and, as previously noted, was found to melt at 91°–92° C. Since in my previous papers no attempt was made to determine the true constitution of this interesting body, it was thought that a little more light upon the subject would not only be interesting but desirable. To gain this information, it was decided to submit the sulphonic acid to the action of oxidizing agents, with the view, if possible, of converting it into a

[1] *Ztschr. Chem.*, *1869*, p. 44.
[2] This Journal, **3**, 111 (*1881*).

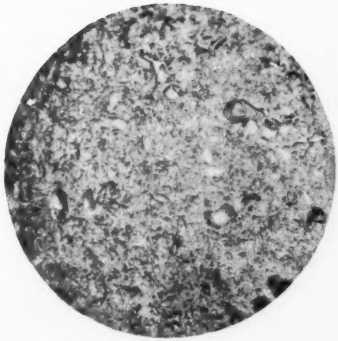


FIG. 1.

FIG. 2.

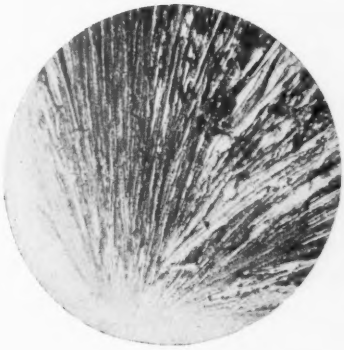


FIG. 3.

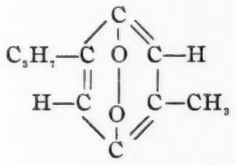
FIG. 4.

FIG. 5.

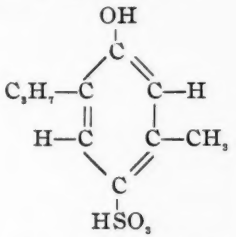
FIG. 6.

quinone, and from it determine the true constitution of the thymolsulphonic acid. For this purpose the following experiment was made :

Ten grams of the sodium salt of alphathymolsulphonic acid were dissolved in 100 cc. of water and to the solution was added a solution of thirty grams potassium bichromate, and ten grams of 66° sulphuric acid in 100 cc. of water. The mixture was now heated under a reflux condenser for about one-half hour and then submitted to steam distillation. A yellow oily liquid of penetrating and peculiar smell, passes over with the steam, and solidifies partly in the condenser and partly in the recipient, to a mass of yellow crystalline leaflets. These after recrystallization from alcohol and water, have the constant melting-point of 45.5°, and unite with hydroxylamine chloride to form a well-characterized oxime. From the above and its general characteristics, it was identified as thymoquinone of the following constitution :



Therefore as in the process of oxidation, the HSO_3 group and OH group are necessarily replaced by the two CO-groups, it follows that the constitution of my thymolsulphonic acid must be represented by the following formula :



That is, the HSO_3 group stands in the para position, in relation to the OH group.

It has also been shown by Ad. Claus,[1] that Engelhardt and Latschinoff's alphathymolsulphonic acid, is a parasulphonic acid, and as my acid is identical with their product, it follows that this is an additional proof of the correctness of the constitutional formula above set forth.

Engelhardt and Latschinoff[2] mention two other isomeric thymolsulphonic acids, which they obtained simultaneously with the para acid, and which they designate as the β- and γ-acid. These are separated from the para acid by the difference in solubility of their potassium salts, the potassium salt of the para acid being much more freely soluble than the potassium salt of the β-acid (according to Claus, the β-acid is the orthosulphonic acid and the γ-acid, a mixture of para and disulphonic acids).

It therefore seemed possible that by my mode of operating, isomeric acids might likewise be formed and to settle this question the following experiment was made :

The mother-liquor separated from the barium salt of thymolparasulphonic acid, was diluted with water, heated to boiling and treated with sufficient potassium carbonate, to precipitate all the barium present, as barium carbonate. The latter was collected upon the filter, washed with hot water and the filtrate concentrated to a small volume by evaporation ; no crystals of a difficultly soluble potassim salt separated on cooling, hence Engelhardt and Latschinoff's β-sulphonic acid or thymolorthosulphonic acid was absent. As a further evidence of the absence of the ortho acid, the above solution was evaporated to dryness, and the dry residue dissolved in ninety per cent. alcohol, in which it is very soluble. On cooling no separation of a difficultly soluble potassium salt occurred and it is only after evaporating the alcoholic solution to the consistency of a sirup and allowing the latter to cool, that I was finally able to obtain the potassium salt in a crystalline form. The product thus obtained crystallizes from alcohol, in rhombic crystals which are freely soluble both in alcohol and water. From water it crystallizes in flat-sided needles. A comparison of this salt, with the potassium salt of thymolparasulphonic acid described by Engelhardt and Latschinoff, shows that they are identical.

[1] *J. prakt. Chem.*, **43**, 334-355.
[2] *Loc. cit.*

The oily product "A" referred to in the early part of this paper, as being formed in small quantity by the action of sulphuric acid on thymol, at 100°, crystallizes on cooling to a white crystalline mass which, when viewed under the microscope, is seen to be composed of a multitude of little white needles (Fig. 6). The product was dissolved in cold water, heated to boiling, and neutralized with barium carbonate. The barium sulphate formed was collected upon a filter, washed with hot water, and the filtrate concentrated to a small volume on the water-bath.

After several weeks' standing a barium salt was obtained which crystallized in long white needles, some of which were two or three centimeters long. The yield of this product was, however, very small, hardly enough for analysis being obtainable. It is exceedingly soluble in water and for this reason is difficult to obtain in a crystalline form. It crystallizes with water of crystallization.

0.3399 gram salt, dried at 100°, lost 11.29 per cent. water.

0.3012 gram salt, dried at 100°, gave 0.1472 gram barium sulphate.

	Theory for $C_6H(CH_3)(C_3H_7)OH\langle^{SO_3}_{SO_3}\rangle Ba + 3H_2O$.	Found.
H_2O	13.53	11.29
Ba	30.78	28.71

From the above it is evident that the barium salt analyzed was not pure, but as the figures obtained agree much better with the theory for a disulphonid acid than anything else coupled with the great solubility of the barium salt, I am inclined to believe that what I had in hand, was a barium salt of thymoldisulphonic acid, which is probably represented by the following formula:

$$C_6H(CH_3)(C_3H_7)(OH)\langle^{SO_3}_{SO_3}\rangle Ba + 3H_2O.$$

Owing to the small quantity of material at my disposal, a more thorough examination of this salt was impossible.

To recapitulate, it will therefore be seen that the only two products formed by the action of 66° sulphuric acid on thymol, at the temperature of boiling water, are thymolparasulphonic acid and thymoldisulphonic acid, of which the former constitutes by far the greater portion, while the latter product is only obtained in very small quantity.

MOLECULAR WEIGHTS OF LIQUIDS, III.

By Clarence L. Speyers.

Received December 17, 1898.

A SHORT time ago, I published two papers[1] on this subject, using the equation

$$\frac{n_1}{n_1+n_2}=\frac{p-p'}{p},$$

to determine the molecular weights of liquids in homogeneous liquid mixtures. Recently some more measurements of vapor-pressures of solutions have been published[2] to which measurements this equation can be applied.

Using the notation and arrangements of the preceding paper, we get the following two tables:

CCl_4 AND C_6H_6 (50°).

CCl_4 pct. mols.	C_6H_6 pct. mols.	v. p. CCl_4 (310.2).	v. p. C_6H_6 (270.9).	Mol. wt. CCl_4.	m/m_0 CCl_4.	Mol. wt. C_6H_6.	m/m_0 C_6H_6.
10	90	34.0	242.4	148.4	0.97	81.2	1.0
20	80	67.0	215.0	149.3	0.97	85.7	1.1
30	70	98.2	190.0	155.7	1.0	84.0	1.1
40	60	128.6	166.0	162.9	1.1	82.5	1.1
50	50	157.4	140.0	164.9	1.1	79.9	1.0
60	40	187.5	113.0	165.4	1.1	79.0	1.0
70	30	217.0	87.0	170.0	1.1	77.2	1.0
80	20	247.0	60.0	175.2	1.1	75.3	0.96
90	10	279.0	30.6	176.3	1.1	75.8	0.97

CCl_4 AND C_7H_8 (50°).

CCl_4 pct. mols.	C_7H_8 pct. mols.	v. p. CCl_4 (310.2).	v. p. C_7H_8 (93.0).	Mol. wt. CCl_4.	m/m_0 CCl_4.	Mol. wt. C_7H_8.	m/m_0 C_7H_8.
10	90	27.2	85.3	188.8	1.2	79.4	0.86
20	80	54.0	77.4	190.2	1.2	77.4	0.84
30	70	82.4	69.1	190.0	1.2	77.4	0.84
40	60	111.4	60.8	188.4	1.2	77.0	0.84
50	50	143.0	52.0	194.5	1.3	78.3	0.85
60	40	175.4	42.7	195.3	1.3	73.9	0.80
70	30	208.2	33.0	195.9	1.3	79.9	0.87
80	20	240.0	22.7	198.1	1.3	77.9	0.85
90	10	274.0	11.8	200.6	1.3	80.3	0.87

The plots corresponding to these tables are given in Fig. 1.

[1] *Jour. phys. Chem.*, **2**, 347, 362 (*1898*).

[2] Lehfeldt: *Phys. Mag.*, **46**, 42 (*1898*).

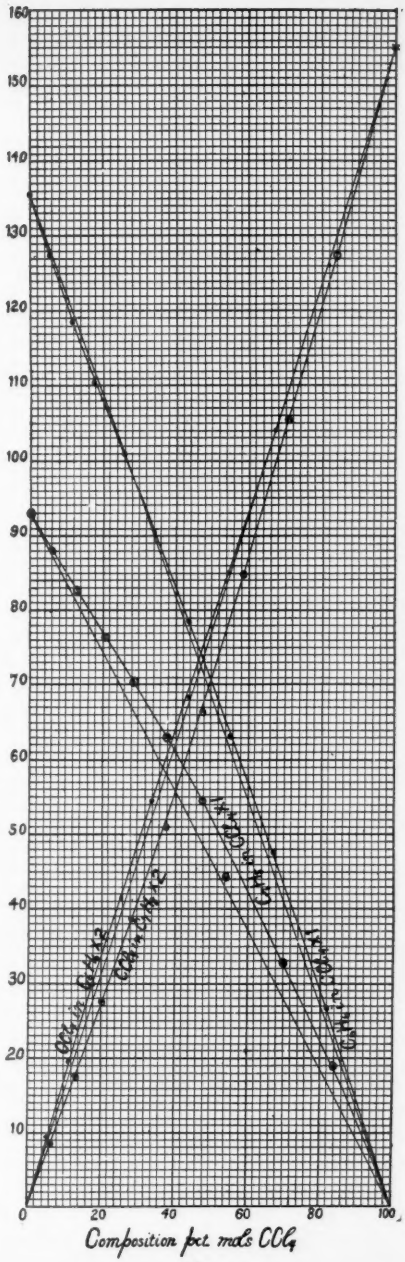

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
20
40
60
80
100
Composition pct. mols CCl_4
Carbon Disulphide
Chloroform
Carbon Tetrachloride
Methylene Chloride

Fig. 1.

The vapor-pressure plot of benzene indicates a slight association of carbon tetrachloride when the mixture is concentrated with respect to carbon tetrachloride, but a slight dissociation when the mixture is dilute with respect to it. In view of the nature of carbon tetrachloride, I think we should take this to mean that carbon tetrachloride has a normal molecular weight when mixed with benzene.

The vapor-pressure plot of carbon tetrachloride indicates a slight dissociation of benzene when the mixture is concentrated with respect to benzene, but not enough to show an association of the benzene molecules. The very peculiar plot given by Linebarger[1] is not found here.

The vapor-pressure plot of toluene indicates an association of carbon tetrachloride, but as there was no indication of association in the experiments of Linebarger, I think we are to conclude that carbon tetrachloride has a normal molecular weight in toluene.

The vapor-pressure plot of carbon tetrachloride would indicate a slight dissociation of toluene, but this is hardly admissible, as here likewise we must conclude that toluene has a normal molecular weight in carbon tetrachloride, particularly since the experiments of Linebarger point to the same conclusion.

C_2H_5OH AND C_6H_6 (50°).

C_2H_5OH pct. mols.	C_6H_6 pct. mols.	*v. p.* C_2H_5OH (219.3).	*v. p.* C_6H_6 (270.9).	Mol. wt. C_2H_5OH.	m/m_0 C_2H_5OH.	Mol. wt. C_6H_6.	m/m_0 C_6H_6.
10	90	110.0	264.4	205.1	4.4	705.0	9.0
20	80	135.0	256.6	206.3	4.5	498.0	6.4
30	70	151.0	248.0	213.5	4.6	401.0	5.1
40	60	164.0	237.4	217.3	4.7	346.0	4.4
50	50	175.0	225.8	230.6	5.0	307.0	3.9
60	40	185.2	207.6	226.3	4.9	281.0	3.6
70	30	194.0	183.0	223.5	4.9	254.0	3.3
80	20	203.2	146.0	215.2	4.7	240.0	3.1
90	10	211.4	96.4	228.8	5.0	226.0	2.9

[1] This Journal, 17, 615, 690 (*1895*); Speyers: *J. phys. Chem.*, 2, 347 (*1898*).

C_2H_5OH AND C_7H_8.

C_2H_5OH pct. mols.	C_7H_8 pct. mols.	v. p. C_2H_5OH (219.5).	v. p. C_7H_8 (93.0).	Mol. wt. C_2H_5OH.	m/m_0 C_2H_5OH.	Mol. wt. C_7H_8.	m/m_0 C_7H_8.
10	90	110.0	86.8	71.6	1.6	831.0	9.0
20	80	135.0	83.0	95.5	2.1	588.0	6.4
30	70	150.6	80.5	127.0	2.8	469.0	5.1
40	60	162.2	77.8	157.0	3.4	390.5	4.2
50	50	169.6	75.2	194.3	4.2	312.7	3.4
60	40	174.4	71.9	235.1	5.1	237.1	2.6
70	30	179.0	66.8	273.7	5.9	174.3	1.9
80	20	187.8	57.3	295.4	6.4	136.2	1.5
90	10	203.6	36.9	272.2	5.9	130.9	1.4

The plots corresponding to these two tables are given in Fig. 2. We see from the vapor-pressure of alcohol that benzene and toluene are polymerized to a remarkable degree in alcohol, and very equally so from a concentration of 100 per cent. gram-molecules of benzene or toluene down to about sixty per cent. gram-molecules benzene or toluene, but from about sixty per cent. gram-molecules of these two liquids down, they are not equally polymerized in alcohol. The vapor-pressure plot of alcohol with toluene runs so as to indicate a normal molecular weight for toluene in alcohol when the mixture is dilute with respect to toluene, but the vapor-pressure plot of alcohol with benzene does not indicate a normal molecular weight for benzene at any dilution.

We see from the vapor-pressure plot of toluene that alcohol is highly polymerized in toluene, but when the concentration of the toluene is high, the molecular weight of the alcohol drops towards a normal value. This corresponds to the behavior of toluene in alcohol.

The vapor-pressure plot of benzene, however, indicates that alcohol is highly polymerized in benzene at all concentrations. This corresponds to the behavior of benzene in alcohol. On the other hand, there is a possibility that alcohol has a normal molecular weight in benzene when the mixture is dilute with respect to alcohol, for there are two observations of the vapor-pressure of benzene at about 125 mm. mercury, which lie very

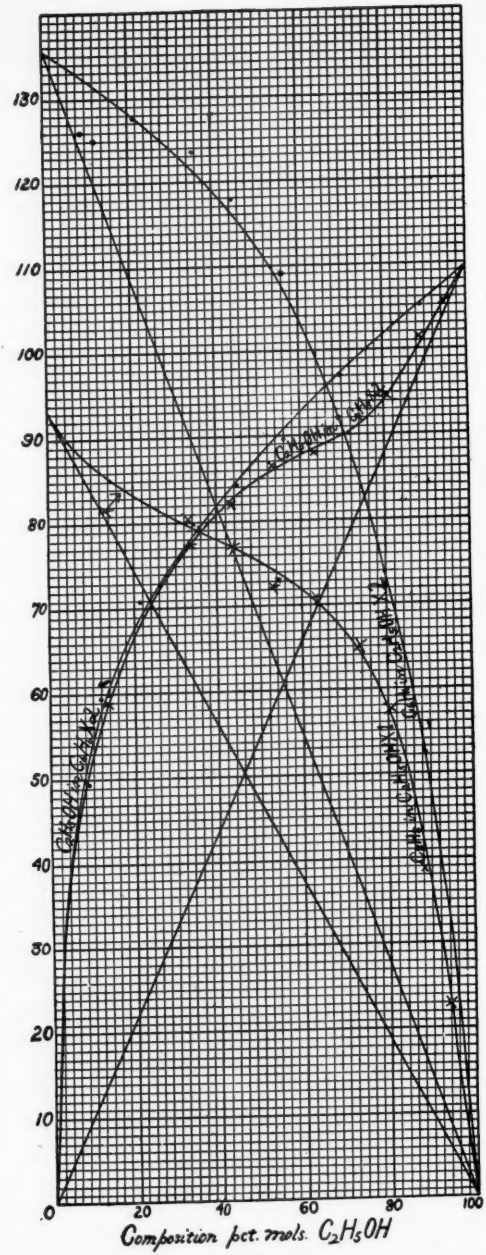

130
120
110
100
90
80
70
60
50
40
30
20
10
0
20
40
60
80
100
Composition pct. mols. C_2H_5OH

Fig. 2.

close to the diagonal. If these observations are correct, then alcohol would have nearly normal molecular weights at the concentrations corresponding to these observations, but these observations are so different from the other ones that I thought it best to draw the plot as I did.

RUTGERS COLLEGE, December 16, 1898.

A NEW FILTERING MEDIUM.[1]

BY GEO. WM. SARGENT AND JNO. KIRK FAUST.

Received November 23, 1898.

FOR the removal of manganese dioxide from the nitric acid in which solution it has been precipitated by potassium chlorate, a glass tube similar to that used for carbon determinations, is recommended. The bottom of this tube is covered first with a small piece of glass wool, then with asbestos. This we used for some time, but were frequently troubled by the precipitate running through, unless a very thick bed of asbestos was made. In this case, the time consumed in filtering was very considerable, due to clogging of the filter by potassium chloride from the large amount of potassium chlorate necessary to oxidize the chromium which was present in considerable quantities in the steels dealt with.

After some experimenting, we adopted the following as giving the most satisfactory results: A carbon filtering tube with a stem five inches long and a body three and one-half inches long and one and one-fourth inches in diameter, is filled one-fourth inch with pewter sand, a small piece of glass wool being used to retain the sand; over this a thin layer of asbestos is formed by pouring in the asbestos shaken up with water and sucking the bed dry. A little hot dilute nitric acid is poured back and forth through the tube several times, when it is ready for use.

When a heavy precipitate is encountered, the bulb from a syringe is used to force air into the tube and drive the liquid through, care being taken to keep the bulb compressed until removed from the tube.

We have found that the quickest and best way to wash the manganese dioxide consists in allowing the nitric acid to run

[1] Read at the New York meeting of the American Chemical Society, December 28, 1898.

entirely through the filter, then washing all the residue in the beaker into the tube with cold water, and as soon as the filter has drained, washing out the potassium chloride with hot water. The filter and manganese dioxide are blown out into the beaker and the dioxide reduced with ferrous sulphate, etc. The sand and asbestos are recovered and used time and again. The washings and nitric acid filtrate were examined and found free from manganese. In this filtrate the chromium was determined by adding ice and reducing the chromate with ferrous sulphate, etc.[1]

This sand filter was used for the removal of ammonium phosphomolybdate from the solution in which it was precipitated. It was found best to place a few pieces of glass rod upon the asbestos to hold it in position when the solution was first being poured upon the filter. With this device, we have found the freeing of the precipitate and filter of molybdic acid to be more easily and more quickly accomplished than when paper filters were used. The phosphomolybdate has a tendency, as all know, to 'creep,' and, unless the filter is fitted properly to the funnel, to get into the filtrate. This trouble is avoided by the sand filter. To dissolve the precipitate, the ammonia solution is poured through the filter two or three times and finally washed out with hot water. A number of determinations, using the sand and paper filters side by side, have been made on the same sample and the results obtained agreed to a thousandth. It was found best to wash the sand filters, used to catch the ammonium phosphomolybdate, with ammonia as well as with nitric acid, since in the ammonia washings silica and alumina were found, and these would tend to clog the reductor.

Once made up, they stand ready for repeated use, and besides saving time they save considerable money, especially where many determinations are made. By these filters, one man was able to turn out in one day forty-two phosphorus determinations, and every precipitate was washed until the droppings from the tube gave no reaction for molybdenum when tested with ammonium sulphide.

The cut shows clearly the manner of making up these filters.

CHEMICAL LABORATORY, CARPENTER STEEL CO.,
READING, PA.

[1] "Methods for the Analysis of Ores, Pig Iron, and Steel," compiled from the Transactions of the Chemical Section of the Engineers' Society of Western Pennsylvania.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

SILICA AND INSOLUBLE RESIDUE IN PORTLAND CEMENT.

BY P. W. SHIMER.

Received February 14, 1899.

IT is desired, in this brief note, to call attention to a possible source of error in the determination of silica in cement, as usually carried out in many laboratories. In the method almost universally used the steps are as follows: Solution, with careful stirring, in either hydrochloric acid alone, or with addition of nitric acid; evaporation to dryness; solution, filtration, and ignition of the siliceous residue, without treatment with hydrofluoric acid. The insoluble residue is calculated as silica. The results are claimed to be accurate to within 0.20 per cent., and it is no doubt true, as claimed, that it is not possible to get duplicate samples of cement from the same bins, in which the average disagreement will be less than this. If the error in the silica determination were no greater than 0.20 per cent., it would not, practically, be important.

The writer has recently met with four samples of Portland cement in which the differences between the silica determined by solution in hydrochloric acid and by the fusion method were 2.48, 2.46, 1.10, and 1.00 per cent. If the silica determined by the acid method were treated with hydrofluoric acid, there is no doubt the results by that method would be sufficiently accurate.

In the case where there was a difference of 2.48 per cent. between the silicas by the two methods, we have complete analyses of the cement by each method of solution. The silica by the acid method was 2.48 per cent. high, while all the other determinations were correspondingly lower than the determinations by the fusion method. Alumina was 1.24 per cent. low; ferric oxide was 0.64 per cent. low; lime, 0.28 per cent.; magnesia, 0.12 per cent.; and sulphur trioxide was 0.14 per cent. low. The total of these differences is 2.42 per cent., thus showing conclusively to what the contamination of the silica by the acid method was due.

The discrepancies in the other three analyses are similarly accounted for. The excess of 2.46 per cent. in the silica by the

acid method in the second sample, is balanced by a deficiency of 2.30 per cent. in the other determinations. The excess of 1.10 per cent. in the silica by the acid method in the third cement, is balanced by a deficiency of 0.96 per cent. in the other determination.

The excess of 1.00 per cent. in the silica by the acid method in the fourth cement, is balanced by a deficiency of 1.12 per cent. in the other determinations. It is interesting to note, in this connection, that the physical tests of the first two samples of cement, which showed differences of 2.48 and 2.46 per cent. between the two silicas, showed marked inferiority as compared with the two samples in which the differences between the silicas were 1.10 and 1.00 per cent.

This would point to insufficient clinkering or sintering of the first two cements. In other words, the burning of the cement was not at a high enough temperature, or was not continued long enough to completely decompose the insoluble silicates of alumina and to convert them into silicates and aluminates decomposable by hydrochloric acid. I have no doubt whatever, that when a Portland cement is properly compounded and correctly burned, the silicates and aluminates are easily decomposable by hydrochloric acid, and therefore the silica may be determined with very close approximation to the correct figures by the acid method. On standard cements, of good reputation, I have never found a greater difference than 0.20 per cent. between the silicas by the two methods. However, when the cement is not properly compounded and correctly burned, there will be a notable difference between the two silicas. The determination of silica by the two methods would thus appear to furnish an excellent means of getting valuable information as to the quality of the cement. When the two silicas agree, it means that all silicates and aluminates are decomposed by hydrochloric acid, and therefore are in an active hydraulic condition. When there is a large difference between the two silicas, it means the presence in the cement of unconverted and inert silica and alumina. In other words, the clay matter that the burning should have converted into active hydraulic combinations with lime, remains unconverted and inert.

In a sample of natural cement of low grade the silica by fusion

was 26.90 per cent.; by the acid method it was 31.45 per cent., a difference in this case of 4.55 per cent., proving conclusively that, while the acid method may be very useful when used by an experienced chemist at a cement works making regularly a uniform product, it is not at all to be relied on as a universal method to be used indiscriminately for the determination of silica in all cements.

[CONTRIBUTIONS FROM THE UNITED STATES LABORATORY, BOSTON, MASS.]

ANALYTICAL RESEARCH ON SOD OIL.

BY ERASTUS HOPKINS, D. L. COBURN, AND EDW. SPILLER.

Received November 3, 1898.

EXCEPTING among the tanners very little is known of this oil, and among them it is known only in its principal application. Its chemical properties are little known and the aim of this paper is to state the main chemical facts regarding this oil, thousands of tons of which are used each year in the currying of leather.

To better understand what sod oil is, let us say that it is an oil which has for its basis various non-drying oils and greases, but almost exclusively cheap fish oils. These oils are put into the leather for currying purposes and the excess is extracted by various methods. The extracted oil has undergone a change from the original oil by coming in contact with the leather and becomes what is known in commerce as 'sod oil,' more highly valued by the tanners than the original oil.

In "Oils, Fats and Waxes," Benedikt and Lewkowitsch describe this oil as follows: "Sod oil or dégras is the waste fat obtained in the chamoising process and is used for currying purposes; *i. e.*, dressing bark-tanned leather." Dégras proper might be said to be the oil obtained from skins in the manufacture of chamois leather, while its allied substance, sod oil, is the oil obtained from ordinary leather.

The principal oils used from which to make sod oil are menhaden and cod oils, but various oils (even olive oil) and greases may be used, and hence give to the sod oil a variation in constants which have so extended a range that they might not be constants at all.

Sod oil has the odor of leather and is generally of such a character that it forms a separating emulsion. The color may be a light yellow to a dark brown. Its viscosity may vary from that of a pure oil to a thin grease with a specific gravity of from 0.96 to 0.99.

The noticeable chemical characteristics are the presence of a so-called 'dégras former' hide fragments, and a high ash content due to the leather from which the oil is extracted. Another point of interest is the great variation in moisture and mineral acid of the oil, as well, of course, as of all its constants.

It is claimed that the higher the percentage of 'dégras former' and the lower the percentage of mineral acid, the more valuable the oil, but commercially the price of the oil does not seem to be governed by these facts, but is bought and sold on firm names, which is undoubtedly due to the fact that tanners still work by the "thumb rule" rather than by being advised by scientific research.

We hope in this paper to bring out the general analytical facts regarding the oil itself and later to work up the almost unknown dégras former which is described as a resinous substance (not a resin) found in sod oil, melting at 65°–67°, and showing certain degrees of solubility with various solvents. Dégras former, as it occurs in sod oil, can be extracted from sod oil by petroleum ether, but in its pure state dégras former is insoluble in this menstruum.

Sod oil contains unsaponifiable and saponifiable oil, the unsaponifiable being undoubtedly due to the unsaponifiable matter in the fish oil used. It contains also moisture, soap and hide fragments, ash and dégras former, and we have endeavored to find a rapid process by which moisture, oil, soap, and hide fragments could be determined which will be described below under that subject. The samples of sod oil taken were commercial and imported sod oils.

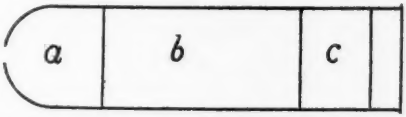
MOISTURE, OIL, SOAP, AND HIDE FRAGMENTS.

After some preliminary work on the determination of moisture, oil, soap, and hide fragments, it was found that the methods described by Benedikt and Lewkowitsch were rather tedious, and the results in our hands were unsatisfactory. This was

particularly true of the moisture which we attempted to determine by weighing the oil with pure ignited sand (enough to absorb it), and by drying at 120° C. in a drying oven. We were unable to get a constant weight by this method, the oil continuing to lose weight even after five or six days drying.

The following method was then devised and found to give accurate results:

For the analyses we used a test-tube of sixty to eighty mm. in length and fifteen to twenty mm. in diameter with a small hole blown in its bottom, and furnished with a platinum wire for suspending the tube while weighing. A small wad of absorbent cotton is first inserted into the tube (*a*), then an ashless filter paper of twelve cm. diameter is folded about the finger (placing the tip of the finger in the center of the paper) and placed in the test-tube so that upon withdrawing the finger from the inside of the filter-paper, the paper with its closed end on the cotton wad takes the shape of the test-tube and forms a filter-paper capsule which prevents the solid matter of the oil from being mechanically carried through the cotton. The capsule is made of filter-paper because it was found that the ordinary capsule is



too large and heavy for this work. The inside of this filter-paper capsule is filled with closely rolled ashless filter-papers (*b*) and a cotton wad is put on top (*c*). This is dried and weighed for tare. The upper wad is then removed and the sod oil introduced and absorbed by the filter-paper, care being taken that the oil does not saturate the lower cotton wad. The upper wad is then replaced and the weight taken gives the charge of oil. The test-tube after weighing is placed in a water-jacket drying-oven and attached by the lower end of the tube to a suction-pipe which, under slight pressure, draws hot air through the test-tube from the top, out through the hole in the bottom. By using a water-jacket oven the temperature is ensured to remain constant at 100° C. and the suction of hot air makes the drying to constant weight rapid when compared to other methods used for the

drying of oils. The loss in weight gives the moisture. The tube containing the anhydrous oil is placed in a Soxhlet apparatus, and the oil is extracted by 40° petroleum-ether. A weight taken on the dried tube, or better on the extracted oil, gives the oil, etc., soluble in petroleum-ether. There are now left in the tube soap, hide fragments, and ash. The test-tube is next treated in the Soxhlet with alcohol which extracts the soap. A weight on the tube gives (1) by loss, soap, etc., soluble in alcohol, (2) hide fragments and ash insoluble in petroleum-ether and alcohol, and upon igniting the cotton and filter-paper this ash is determined and the difference gives the amount of hide fragments.

The ash found is lower than total ash, and this difference is accounted for by finding fractions of the ash in the oil and soap. For absolutely accurate analytical work the ash soluble in petroleum-ether and alcohol should be determined and subtracted from the oil and soap and added to the ash of ignition, but the error is so small that for commercial work this can be omitted as we have omitted it in this research. Upon making determinations of these ash fractions we have found that their sum checks the total ash. All of these determinations are made upon one charge which is an advantage in itself.

The process is rapid and gives very accurate results, and its use is not in any way confined to sod oil, but may be used in the analysis of all oils and greases where drying and extraction are required. Because of the necessarily small test-tube used we found that a Soxhlet apparatus with a two-inch siphon tube instead of the regulation four-inch tube was better adapted to the work.

TOTAL ASH.

This is determined by igniting the oil in a tared platinum dish. The ash is found to be high, and consists chiefly of calcium, iron, and the alkalies for bases with carbon dioxide and sulphur trioxide for the acid radical. The calcium comes from the lime used in liming hides.

DÉGRAS FORMER.

For this determination Jean's method, mentioned by Benedikt and Lewkowitsch, was followed except in certain modifica-

tions, which we found to be necessary because of the lack of concordant results. His method advises decantation of the liquid from the crust of dégras former: this we found inaccurate because by decantation small particles of dégras former were carried away, and for this reason we used a filter and transferred the crust of dégras former upon the filter. Another point which he omits to state is that oil often adheres to the dégras former and thus causes too high results; this we obviated by washing the dégras former with petroleum-ether after having washed it free of acid and salt. Jean dissolves the dégras former in ether but we found that it took too long and too much solvent, whereas it is readily soluble in absolute alcohol and gives a pure product melting at the required temperature.

Our modified Jean's method is as follows: The oil is saponified according to the method for the determination of unsaponifiable matter. (The unsaponifiable number may thus be determined on the same charge.) The saponifiable matter of the sod oil which contains the easily saponifiable dégras former, is heated to drive off the alcohol and ether used in the saponification. The saponifiable matter is taken up with water, and the soap is precipitated hot with an excess of salt. The mixture is cooled and filtered off into a beaker and hydrochloric acid is added to the filtrate. The dégras former is precipitated by hydrochloric acid in flocks which unite on boiling and adhere to the sides of the beaker on cooling, leaving a soft brown crust on the top of the solution. The liquid is filtered off (filtering being used rather than decantation to prevent loss); the dégras former is washed with water free from acid and salt and then with petroleum-ether free from oil. It is then dissolved on the filter with absolute alcohol; the alcohol is driven off and the dégras former weighed. This dégras former should melt at 65°–67° C.

GENERAL ANALYTICAL TESTS.

The analytical tests, common to oil analysis, and made by us with only a few modifications, were the determinations of total KOH, mineral acid, total acid, from which were calculated the KOH number, ether number, and free fatty acid number, also of Reichert-Meissl, iodine value, unsaponifiable, and iodine of unsaponifiable. All of these were calculated to anhydrous sod

oil and also to numbers "In terms of oil, etc., soluble in petroleum-ether." The methods are so generally well known that they are not given excepting where modifications of the same were found advisable.

The total KOH was determined upon two and one-half grams of the oil and the final titration was made with half-normal hydrochloric acid with phenolphthalein as indicator. It is rather difficult to determine the end-point in these oils because of the high color of the oil, but if, when the end-point is near, the flask is vigorously shaken a foam will appear on the surface of the liquid. If a drop of phenolphthalein is now added, the foam will become pink until the neutral point is reached. The calculation is to milligrams of potassium hydroxide per one gram of sod oil.

The mineral acid was determined by boiling in distilled water two to two and one-half grams of the sod oil and washing on a filter with hot distilled water until all the mineral acid was removed. This is titrated with standard sodium hydroxide and calculated to milligrams of potassium hydroxide per one gram of sod oil.

The total acid was determined by dissolving two grams of oil in hot methyl alcohol in which all the free acid has been neutralized. This alcoholic solution is titrated with standard sodium hydroxide and calculated to milligrams of potassium hydroxide per one gram of sod oil.

The KOH number is calculated as the difference between the total KOH and mineral acid.

The ether number is calculated as the difference between total KOH and total acid.

The free fatty acid is calculated as the difference between the total acid and mineral acid.

The Reichert-Meissl value, iodine number and unsaponifiable number were determined by the common methods with no modifications.

The petroleum-ether used throughout these experiments and analyses was 40° naphtha which as a separating medium was found to be essential, and as a solvent acted more rapidly and with better results than the lower fractions of naphtha.

The numbers obtained by the above methods differ very

Sod oil.	Total ash.	Moisture.	Oil, etc., soluble in petroleum-ether.	Soap, etc., soluble in alcohol.	Hide fragments.	Ash insoluble in petroleum-ether and alcohol.	Total.	Dégras former.			1. Total KOH.		
								Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.	
1. Yellow	0.96	25.27	72.60	1.90	0.66	0.12	100.55	0.93	1.24	1.28	99.07	132.57	136.46
2. Brown	0.70	3.38	88.61	7.05	1.05	0.15	100.24	15.98	16.54	16.91	206.51	213.73	233.05
3. Brown	0.215	2.75	96.60	1.32	1.09	0.16	101.92	2.73	2.81	2.83	111.52	114.67	115.44
4. Yellow	0.05	19.48	....	....	....	....	....	....	....	....	108.75	135.06	.....
5. Brown	1.045	15.45	75.37	7.24	1.26	0.47	99.79	6.33	7.48	8.39	140.59	166.26	186.53
6. Yellow	0.68	30.87	59.74	8.81	0.49	0.06	99.97	2.65	3.84	4.43	85.70	123.97	143.46
7. Brown	0.37	4.59	89.59	3.09	2.99	0.15	100.41	21.41	22.44	23.89	181.53	190.05	202.40
8. Brown	0.77	33.46	58.81	5.40	2.24	0.35	100.26	17.73	26.64	30.14	135.83	204.13	230.96
9. Brown	0.55	1.01	95.69	2.44	0.79	0.13	100.06	13.91	14.05	14.53	186.53	188.43	194.93
10. Brown, thick.	0.36	40.61	56.62	3.19	0.31	0.22	100.95	0.65	1.09	1.15	64.04	107.83	113.10
11. Brown, thin ..	0.28	3.94	94.38	2.57	0.15	0.16	101.20	2.74	2.85	2.90	101.48	105.64	107.32
12. Brown	0.46	23.70	73.36	0.68	1.29	0.15	99.18	8.41	11.02	11.46	109.94	144.09	149.86

Sod oil.	2. Mineral acid.			3. KOH number. 1—2=3.			4. Total acid.			5. Ether number. 1—2=3.		
		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.
1. Yellow.....	20.77	27.79	28.62	78.30	104.78	107.84	48.20	64.50	66.39	50.87	68.07	70.07
2. Brown.....	3.16	3.28	3.56	203.35	210.45	229.49	75.80	78.48	85.54	130.70	135.28	147.51
3. Brown.....	1.63	1.67	1.68	109.89	113.00	113.76	46.32	47.63	47.95	65.20	67.04	67.49
4. Yellow.....	1.07	1.33	....	107.68	133.75	....	27.20	33.78	....	81.55	101.28	....
5. Brown.....	0.96	1.13	1.27	139.63	165.13	185.26	74.14	87.69	98.37	66.45	78.57	88.16
6. Yellow.....	24.07	34.82	40.29	61.63	89.15	103.17	57.06	82.54	95.51	28.64	41.43	47.95
7. Brown.....	64.77	67.88	72.29	116.56	122.17	130.11	84.17	88.22	93.95	97.16	101.83	108.45
8. Brown.....	52.54	77.96	89.34	83.29	126.17	141.62	70.50	105.95	119.88	65.33	98.18	111.08
9. Brown.....	90.50	91.51	94.57	96.03	96.92	100.36	124.50	125.77	130.11	62.03	62.66	64.8_2
10. Brown, thick.	7.70	12.96	13.60	56.34	94.87	99.50	55.21	92.96	97.51	6.83	14.87	15.59
11. Brown, thin..	22.20	23.11	23.52	79.28	82.53	84.00	61.83	64.37	65.51	39.65	41.27	41.81
12. Brown.....	10.58	13.86	14.42	99.36	130.23	135.44	30.90	40.49	42.12	79.04	103.60	107.74

Sod oil.	6. Free fatty acid. 1 − 4 = 5			Reichert-Meissl number.			Iodine number.			Unsaponifiable number.			
		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.		Anhydrous.	In terms of oil, etc., soluble in petroleum-ether.	Iodine of unsaponifiable.
1. Yellow	27.43	36.71	37.77	1.87	2.50	2.58	52.45	70.18	73.76	20.60	27.56	28.39	31.76
2. Brown	72.64	75.17	81.98	2.66	2.75	3.00	60.54	62.66	68.32	0.95	0.97	1.07	9.38
3. Brown	44.69	45.96	46.27	2.53	2.60	2.69	43.56	44.79	45.01	41.46	42.62	42.92	16.89
4. Yellow	26.13	32.45	....	2.24	2.66	....	55.02	68.33	....	18.95	23.53	....	22.48
5. Brown	73.18	86.56	97.10	2.41	2.85	3.19	46.69	55.22	61.94	14.90	17.62	19.77	20.80
6. Yellow	32.99	47.72	55.22	1.35	1.95	2.26	49.03	70.92	82.07	14.99	21.68	25.09	23.66
7. Brown	19.40	20.34	21.66	1.66	1.74	1.85	59.06	61.90	65.92	0.58	0.61	0.64	3.22
8. Brown	17.96	27.99	30.54	3.72	5.59	6.32	44.17	66.38	75.11	2.80	4.21	4.76	52.07
9. Brown	34.00	34.26	35.54	2.58	2.61	2.69	77.53	78.32	81.02	0.37	0.37	0.38	71.58
10. Brown, thick	47.51	80.00	83.90	2.02	3.41	3.56	22.79	38.37	40.25	21.81	36.72	38.52	13.80
11. Brown, thin	39.63	41.26	60.48	2.33	2.43	2.47	47.19	49.12	50.00	29.85	31.07	31.63	25.19
12. Brown	20.32	26.63	27.70	3.87	5.07	5.27	41.01	53.74	55.90	6.32	8.28	8.61	20.95

widely, as can be seen by the accompanying tables, and this is true whether the numbers are referred to the anhydrous sod oil or to the "oil, etc., soluble in petroleum ether." Calculations were also made in terms of "oil, etc., soluble in petroleum-ether less dégras former," but as no concordant results were obtained we did not think it necessary to add another column of figures.

The reason for this variation in figures seems to be the great variety of oils which are used for the making of sod oil as well as the different modifications of treating the same initial oil by different makers. Still, sod oil, by a complete analysis as described above, can be easily distinguished from other oils.

CORRESPONDENCE RELATING TO THE BERZELIUS MEMORIAL SERVICES.

Held in Stockholm, Sweden, October 7, 1898, on the occasion of the fiftieth anniversary of the death of Berzelius.

" *The American Chemical Society:*

Messieurs, chers et honorés collègues: À l'occasion du cinquantieme anniversaire de la mort de Berzelius, l'Académie des Sciences de Stockholm, la Faculté de Médicine de Stockholm (Karolinska Institutet), l'Académie d'Agriculture et la Société des Médecins de Suède se proposent de célébrer la memoire du grand savant par une fête commémorative.

Au nom de ces institutions nous avons l'honneur de vous prier de bien vouloir déléguer un de vos membres pour prendre part à cette solennité, qui aura lieu à Stockholm le 7 octobre 1898.

Veuillez, messieurs et chers collègues, agréer l'assurance de nos sentiments les plus distingués.

A. E. NORDENSKIOLD,
L. F. NILSON,
F. LENNMALM,
CHRISTIAN ZOVEN,
SEVERIN JOLIN.

"551 PUTNAM AVE., BROOKLYN, N. Y.,
September 30, 1898.

DR. A. E. NORDENSKIOLD, Academy of Sciences, Stockholm, Sweden.

Dear Sir: I have the honor to acknowledge the receipt of the communication sent by yourself and colleagues announcing the solemnities in commemoration of Berzelius, on the occasion of the fiftieth anniversary of his death, to be held in Stockholm,

October 7, 1898, under the auspices of the Academy of Sciences of Stockholm, the Faculty of Medicine of Stockholm (Karolinska Institutet), the Academy of Agriculture, and the Medical Society of Sweden.

Permit me also to acknowledge with thanks the request that the American Chemical Society send one of its members as a delegate to take part in this memorial occasion, and to express regret that at the present time none of our members are available as active delegates from the United States. I take pleasure in informing you, however, that honorary delegates have been chosen to represent the American Chemical Society, and to prepare a suitable memorial.

The chemists of America would vie with those of the old world in paying their tribute of reverence to the name and fame of Berzelius, and in recognizing his distinguished services to chemistry and kindred sciences. While no one from this country may be able to participate actively in the solemnities, we would nevertheless not allow the occasion to pass without expressing our great interest in it, and the profound feelings which it awakens among the chemists on this side the Atlantic.

The following named are the members appointed as honorary delegates to represent the American Chemical Society:

WOLCOTT GIBBS, *Chairman*,[1]
GEORGE F. BARKER,
WILLIAM MCMURTRIE,
HARVEY W. WILEY,
ALBERT B. PRESCOTT,
F. W. CLARKE,
J. W. MALLET.

Very respectfully yours,

ALBERT C. HALE,
Secretary of the American Chemical Society."

The following cablegram was sent in time to be received at the meeting:

October 6, 1898.

"To A. E. NORDENSKIOLD, Academy of Sciences, Stockholm, Sweden.

The American Chemical Society reveres the memory of Berzelius who conferred luster on our science.

CHARLES E. MUNROE, *President.*
ALBERT C. HALE, *Secretary.*"

[1] The Committee is given here as finally constituted.

NOTE.

A Method for Cleansing Burettes.—Globules of liquids may adhere to the inner walls of burettes, when they are emptied. The tendency can be removed by allowing a weak solution of chromic acid to stand in the burette for a few hours.

The solution may be made by adding ten grams of potassium bichromate to fifty cc. water and five cc. concentrated sulphuric acid. Pour it in the burette and allow it to remain over night. The solution does not injure the rubber tube of a Mohr burette. Wash the burette well with water. WILLIAM GLENN.

NEW BOOKS.

CHEMISCHE TECHNOLOGIE AN DER UNIVERSITÄTEN UND TECHNISCHEN HOCHSCHULEN DEUTSCHLANDS. By DR. FERDINAND FISCHER, University of Göttingen. Braunschweig: Friedrich Vieweg und Sohn. pp. 54. Price, M. 1.25.

In 1897 Dr. Fischer published "Das Studium der technischen Chemie an der Universitäten und technischen Hochschulen Deutschlands, und das Chemiker-Examen," in which he set forth the status of the subject at that time. The present pamphlet is intended merely as a supplement to that work. It consists of abstracts of addresses, papers, and published articles by leading authorities of Germany, with comments by the author (Fischer) upon some of the articles.

Chemical technology was first included in a university course at Göttingen in 1766 and within a few decades nearly all the universities included it as a major course. For many years at Giessen, Liebig lectured on the subject; an interesting program of the chemical course there, for the years 1809 to 1852 inclusive, is given. With the establishment of the Technische Hochschule, technical chemistry gradually disappeared as a major course in the universities, the last full professor in this subject being Prof. Wagner of Würzburg, who died in 1880. At the present time, in nearly one-half of the German universities, the subject is not taught, but a movement is now on foot to reestablish it and one of the objects of this book is to further the movement.

The state examination of technical chemists is also discussed and apparently much difference of opinion exists among the leading chemists as to its desirability. But nothing seems to have come of the agitation in its favor, and further action on the question is indefinitely postponed. The book closes with a

statement of the purposes of the "Association of Laboratory Directors, etc.," and the regulations adopted to govern examinations for diploma and doctor's degree. F. H. THORP.

LABORATORY WORK IN PHYSIOLOGICAL CHEMISTRY. By FREDERICK G. NOVY, Sc.D., M.D., Junior Professor of Hygiene and Physiological Chemistry, University of Michigan. Second Edition, Revised and Enlarged. Ann Arbor: George Wahr. 1898. pp. 326. Price, $2.00.

The second edition of this work is wholly rewritten, and is practically a new book. It contains directions for laboratory work covering the various food-stuffs and the fluids and secretions of the body, together with brief explanatory descriptions of these substances, and is designed to guide the student in the experimental study of chemistry in its broad relations to physiology, hygiene, and disease. In the latter part of the work, about sixty pages are devoted to quantitative analysis. The experiments and subject-matter are well selected and concisely described without omitting important details. The course may be covered by a class devoting a half-day, daily, for three months to the work. The book will be found useful both in undergraduate college courses and in the medical school where a well-equipped laboratory is at the command of students and teacher.

A noticeable defect in the application to clinical use of the methods taught is the omission of definite information regarding physiological variations. Thus, on page 295, we read, "There is an excess of phosphates in the urine in inflammatory diseases of the nervous system and in rickets and osteomalacia. There is deficiency in indigestion and in structural diseases of the kidney;" and again, "A quantitative analysis will show the presence of an excess or deficiency of phosphates." In describing phosphoric acid in urine, the text states "On an average 2.5 g of P_2O_5 are excreted per day." What variation, then, from this amount is to be considered an excess or deficiency? The author does not state. If the determination is to serve any practical purpose, evidently some more definite method of interpretation of the result obtained must be available. This is likewise true of the amounts of the constituents of the gastric juice, breast milk, etc., as well as of urine. Information along these lines is looked for and best taught with the technical methods to be employed.

Prof. Novy's work marks a distinct advance in a field, the

future of which is as promising as that of any department of experimental physiology and medicine. His work is a foremost laboratory guide in a subject demanding a place in the curriculum of every medical school which undertakes to instruct its students in the technic of modern scientific medicine.

E. E. SMITH.

ELECTROLYSIS AND ELECTROSYNTHESIS OF ORGANIC COMPOUNDS. By DR. WALTHER LÖB, Privatdocent in the University of Bonn. Translated by H. W. F. LORENZ, A.M., Ph.D., Graduate of the University of Berlin. New York: John Wiley and Sons. Price, $1.00.

This unpretentious little volume gives, in the space of about 100 pages, what may be fairly termed the substance of all that has been accomplished by the electric current in the domain of organic chemistry. The most recent views in regard to reductions and oxidations are given in sufficient detail to satisfy the inquiring student. The first half of the book considers the aliphatic compounds, the second half the aromatic derivatives. It must be remarked, however, that the completeness of such works as those of Tommasi and of Peters is not found here, although the essentials and the latest results are everywhere present. It is a most suggestive compilation and the student, eager to take up problems in this comparatively new field of research, will find hints upon almost every page as to lines of investigation, which would amply repay his experimental inquiries. Not as a criticism, but simply to arrest an erroneous notion the reviewer would call attention to a statement made on page 18, relating to the electrolysis of metallic acetates. It is there said of uranium acetate that from its solution the current separates the metal, which passes to the anode. This is wrong. Metallic uranium cannot be obtained in this way. It is the hydrate which is deposited at the cathode. Again, on page 25 occurs the sentence "on this property depends the great importance of oxalic acid in quantitative electrolytic analysis, into which it has been introduced by Classen." Would it not be just as well to credit Parodi and Mascazzini with having first applied oxalic acid in this way? They first used this acid in the electrodeposition of iron, after which Classen extended its use by the elaboration of methods for the electrolytic determination of other metals. The closing paragraph of the book calls attention to the "important

points which promise to be of great assistance ... in connection with future research in the field of organic chemistry; ... the oxidation reactions which occur in the electrolysis of acids of the aliphatic series, the reduction reactions in the case of the aromatic series, and lastly the reactions involving substitutions. ... Of these the first is apparently the most promising." The translator has performed his task with great credit to himself.

The reviewer has read the book with pleasure and profit, and is confident that it will be regarded as a welcome addition to our rapidly increasing electrolytic literature.

EDGAR F. SMITH.

MICHAEL FARADAY, HIS LIFE AND WORK. BY SILVANUS P. THOMPSON. New York: The Macmillan Co. 1898. xii + 308 pp. 12mo. Price, $1.25.

The "Century Science Series", of which this volume forms a part, has already issued biographies of Pasteur, Davy, Dalton, and Liebig, as well as of men of science distinguished in other departments than chemistry; but no one of those known to the writer is so charmingly written as that under review. Professor Thompson, it is true, had an uncommon man to portray, simple in his nature and grand in his achievements, and the biographer has most successfully depicted both characteristics. Michael Faraday's life is attractively described by one who sympathizes thoroughly with the gentle, lovable man, and at the same time his scientific work is skilfully reviewed by one well qualified by his own attainments to understand and appreciate it.

In his preface Dr. Thompson refers to the previous biographies of Faraday by Bence Jones, Tyndall and Gladstone, each having special merits, and modestly says "there seems room for another account of the life and labours of the man whose influence upon the century in which he lived was so great", and this volume justifies the remark.

If there be such a thing as the "spontaneous generation" of genius surely Faraday affords a striking example; the son of a working blacksmith and a farmer's daughter, born in humble circumstances in a village near London, receiving very little schooling, serving seven years of apprenticeship to a bookbinder, reaching the age of twenty before he had an opportunity of attending a single lecture on natural philosophy, these condi-

tions would hardly be deemed favorable for producing an intellectual genius, a master in science, whom all peoples on earth delight to honor. That Faraday attained such eminence is plainly due to two controlling factors in his moral nature, an intense love for the truths of nature and indefatigable perseverance, both of which were applied to overcoming obstacles that had baffled many. Faraday's first menial position with the rather haughty Davy, their travels on the continent, which afforded Davy's "valet" so much distress as to partly counterbalance the advantages; Faraday's early studies at the Royal Institution, becoming so noteworthy as to arouse some jealousy in Davy, who, however, soon learned to appreciate the rising philosopher; the simple life of the assistant with his bride in two rooms at the top of the Royal Institution, on £100 a year; his admission into the Royal Society; all these interesting details are narrated in the first two chapters. Then follows an account of the masterly researches in electricity and magnetism, which for convenience is divided into three periods; two chapters are devoted to the circumstances of his later life and to his views on the pursuit of science and on education, and a final chapter deals sympathetically with the religious views of the simple-minded Sandemanian.

Through the pages of the volume are interspersed letters written by Faraday to his intimate friends, facsimiles of the rude sketches of novel apparatus drawn in his note-books, and a few woodcuts of scenes and objects associated with him.

Dr. Thompson remarks that he never ceases to regret that he never met Faraday, but no one of those who did know him has so well portrayed him. A charming portrait of Faraday etched by Dr. Thompson forms the frontispiece to a biography that ought to be studied by every one interested in the development of the physical sciences. HENRY CARRINGTON BOLTON.

TEXT-BOOK OF MEDICAL AND PHARMACEUTICAL CHEMISTRY. By ELIAS H. BARTLEY, B.S., M.D., Ph.G. Fifth Edition, Revised and Enlarged. Philadelphia: P. Blakiston's Son and Co. 1898. 738 pp. Price $3.00.

The demand for a fifth edition of a work is a most substantial tribute to its merit. A quality that has largely contributed to create such a demand, in this instance, is that the subject-matter of Prof. Bartley's work is especially adapted to meet the

requirements of those for whom the book is designed. It is not too voluminous for the medical and pharmaceutical student nor too foreign to his interests.

In Part 1 (about 70 pages) the author presents the fundamental facts of chemical physics. Part 2 (about 40 pages) is devoted to theoretical chemistry, followed in Part 3 (nearly 200 pages) by descriptive inorganic chemistry. The author adopts Mendelejeff's classification of the elements, at the same time retaining the distinction of metals and non-metals. Part 4 (234 pages) is occupied with descriptive organic chemistry, including vegetable and animal proximate principles. The last section of the text, Part 5 (137 pages), is devoted to physiological and clinical chemistry. The author's familiarity with the subject and good judgment in the selection of material are well illustrated in the chapter on foods and diets which contains in less than thirty pages an unusually comprehensive and yet simple presentation of the chemistry of these subjects.

It is to be regretted that the author does not insist upon numerical urinary standards. An attempt to judge of the amounts of various constituents of urine by observing the bulks formed when they are precipitated is of little real value. Such methods are not chemical analysis and have no place in a chemical text-book. Moreover, they rob the clinician of what service a real knowledge might render.

The historical lists of tests for albumin and sugar in urine, which the text records, could with advantage be replaced by descriptions of selected methods. It is the more desirable, in this instance, since these tests are so important and yet confusing to those unaccustomed to urine analysis.

An appendix of twenty pages containing various tables increases the value of the book for reference, while a glossary and complete index render its subject-matter readily available. It is not speaking too highly of Prof. Bartley's work to say that it takes first rank among text-boks on medical and pharmaceutical chemistry. E. E. SMITH.

ESSENTIALS OF MATERIA MEDICA, THERAPEUTICS, AND PRESCRIPTION WRITING. Saunders' Question-Compends, No. 7. By HENRY MORRIS, M.D. Fifth Edition. 288 pages. Philadelphia: W. B. Saunders. Price $1.00.

This little book belongs to a class which has become very

popular with students of medicine in the last ten years, and, like the others, it is arranged in the form of questions and answers. As a matter of necessity the information it presents is very greatly condensed, furnishing often not more than an outline of the subject. It is, therefore, in extent, just about what the student needs and uses when "cramming" for an examination. It is possible that books of this class may be legitimately used, and thus possess for the student a real value, but in general their use is to be regretted as tending to encourage superficial reading. The present book seems to be, in the main, carefully compiled, and as free from error as can be expected with such condensation. A careless statement, or mistake, is found at the bottom of page 203, however, where it is said that potassium salts convert uric acid into the more soluble urea. The accuracy of the statement on page 206, regarding the solubility of lithium urate, is also questionable. J. H. LONG.

A MANUAL OF CHEMICAL ANALYSIS; QUALITATIVE AND QUANTITATIVE. By G. S. NEWTH, F.I.C., F.C.S., Demonstrator in the Royal College of Science. London: Assistant Examiner in Chemistry, Science and Art Department. New York, London, and Bombay: Longmans, Green and Co. 1898. xii + 462 pp. Price, $1.75.

To all who value the previous works by Newth, "Chemical Lecture Experiments," and his two text-books on "Inorganic Chemistry," the appearance of the present manual on analysis will certainly be most welcome. As might naturally be expected from its predecessors, the manual is replete with modern methods of manipulation, clever devices to simplify time-honored reactions, and clear, concise explanations. The fundamental processes of quantitative analysis are accompanied by a wealth of illustration, which should enable the dullest intellect to grasp the successive steps in weighing, filtering, the incineration of filters, the ignition of crucibles, etc. These features could be confidently counted upon in advance.

The plan of the work is of course open to criticism. The qualitative part, which includes a fairly generous treatment of the rarer elements, and less common acids, occupies 188 pages; gravimetric and volumetric quantitative analysis extend also over 188 pages; gas analysis covers 37 pages, ultimate organic analysis, 20 pages; and physico-chemical determinations 10

pages. Whether it is desirable to place a manual of this size in the hands of the beginner in qualitative analysis will be a moot question, in the future, as in the past. Dr. Caldwell has solved the question to some extent in his manual of analysis, limiting the qualitative work to the more common bases and acids, and the quantitative feature to ten or fifteen of the more typical determinations. Frequent editions show that the book has met a distinct need. Dr. Muter and Dr. Long have each published successful manuals on a somewhat more extended scale, providing for medical and pharmaceutical students all necessary qualitative and quantitative instruction in a single volume. The writer doubts the expediency of placing a manual of the nature of Professor Newth's, in the hands of those who have no intention of advancing beyond a course in qualitative analysis. The abundance of detail, and the fact that over one-half of the contents of the book will never be put to practical use, seriously handicap its value for the ordinary college student. On the contrary, he regards it as admirably adapted for the present and prospective needs of such students as take up qualitative analysis as preliminary to more advanced laboratory work in chemistry. For such, the combination in one volume of directions and data covering the whole field of analysis is attended with manifest disciplinary and practical advantages. He has, in fact, not delayed to adopt at once, the manual under consideration, for the use of this category of students in his laboratory.

The arrangement of material is, as a rule, logical and satisfactory. In the qualitative part the important tests for each member of a group of bases, are first given and then the systematic treatment of the group follows, accompanied by a clear scheme. While detail is well worked out, it would seem as if the provision for a more compact and comprehensive survey of the entire field could be improved. Thus on page 16 is the general division of bases into groups; on page 17 is a table of the precipitates given by each group reagent. Group schemes are scattered through the following 160 pages. Then comes, *at the end*, "preliminary tests and operations," forming Chapter XVI. This chapter could advantageously contain a complete schematic summary of all tables given before for the detection of both bases and acids. Such an arrangement, similar to that which gives

such value to the "Tabellen" of Will or Wallach in German, would vastly facilitate the use of Newth's manual for young and unformed minds.

The author has omitted argon and helium from the list of elements, with their atomic weights, and probably wisely, in view of the astonishing group of elementary gases isolated from argon during the past few months. The use of didymium in the same list, and the absence of neodymium, and praseodymium is a bit of conservatism hardly in keeping with the progressive nature of the book.

The number of novel and ingenious devices for carrying out qualitative tests, such as that on page 84 for securing the $CuCl_2$ flame, will render the book most helpful and attractive to young minds. Newth's declination on page 157, to describe odors, is eminently wise and recalls the great amusement which greeted a foreign chemist's recent account of a substance which possessed a "blumenartigen Geruch."

It is to be hoped that our American chemists will follow Newth's example, in adopting the system of standard reagents, devised by Reddrop.[1] In this system all laboratory reagents carry signatures indicating whether they are normal, or multiples or fractions of normal solutions. Thus about one-half of our ordinary reagents are strictly normal, = N; calcium sulphate is $\frac{N}{80}$; sodium hydroxide is 5 N, etc. In this connection Professor Newth could well designate a saturated solution of $Ca(HO)_2$, as $\frac{N}{20}$, and not prefix the qualification "about."[2]

While the manual has so many pronounced features of exceptional excellence it is not free from certain flaws and errors inevitable in a first edition. Thus in the list of reagents just referred to, we miss H_2PtCl_6, $K_2Cr_2O_7$, $NaHC_4H_4O_6$, etc. although directions for their use are given in several places.

Provision is made in this list for a normal solution only of ammonium sulphate, while on page 35, the directions call for a *strong* solution. Among faulty expressions, scarcely admissible in a college text-book, are "*nearly* soluble in alcohol," p. 23; "it is therefore *only* possible to have an aqueous solution of the ortho-acid," note p. 93; "bring the liquid once more *to the boil*,"

[1] *Chemical News*, May, 1890.

[2] Cf. Golding: *J. Soc. Chem. Ind.*, 17, 125.

p. 48. The statements on p. 166 with regard to silicic acid, assigning H_2SiO_3 as the formula of the gelatinous precipitate and H_4SiO_4, as the formula of the soluble acid only, are not in harmony with the results of recent investigations in the writer's laboratory.[1] Both tartaric acid and hydrogen sodium tartrate, are used in testing for ammonium salts (p. 21), but the second reagent only is advised for potassium compounds.

The following omissions of analytical data should be remedied in a second edition; on p. 88, the frequent presence of sulphur in the residue of HgS, $PbSO_4$ and $Hg(NO_3)_2.2HgS$, is overlooked; on p. 70, a method for the separation of glucinum, zirconium, titanium, and uranium should be outlined; on p. 128, no mention is made of Hart's excellent method for mixtures of chlorides, bromides, and iodides; on p. 151, no mention is made of the combustibility of all hypophosphites—their most striking property; on p. 155, no mention is made of the reaction of formates with ferric chloride, nor of the prompt reaction with silver nitrate; on p. 169, the familiar test for silica, etc. by means of calcium fluoride and sulphuric acid is omitted; on p. 151, the deportment of metaphosphates with ammonium molybdate is not stated; on p. 171, pyrophosphoric, metaphosphoric, phosphorous and hypophosphorous acids are omitted from the general scheme for the systematic detection of acids, although such a rare acid as HCNO is included.

Despite these minor blemishes, the book marks a distinct advance in the evolution of the ideal manual of analysis, and will certainly find many friends. THOMAS H. NORTON.

AN INTRODUCTORY COURSE OF QUANTITATIVE CHEMICAL ANALYSIS WITH EXPLANATORY NOTES AND STOICHIOMETRICAL PROBLEMS. BY HENRY P. TALBOT, Ph.D., Professor of Analytical Chemistry in the Massachusetts Institute of Technology. Third Edition, Revised and Enlarged. 153 pp. New York: The Macmillan Co. 1899. Price $1.50.

That a third edition should be demanded in less than two years from the first appearance of this book, is evidence that many teachers have found it suited to their needs. To all the matter contained in the first edition, the present adds the determination of carbon dioxide in dolomite, the determination of silica in laumontite and in feldspar, reference to the determination of zinc

[1] This JOURNAL, 19, 832.

as the pyrophosphate, and a very clear and useful chapter of 17 pages on the theories of solution and some of their applications to analytical chemistry. A note on the capacities of beakers, referred to in the text by numbers, will be appreciated. The paragraphs on temperature of calibration have been rewritten. Of the first edition as an introduction to the principles and practice of quantitative analysis, the present reviewer wrote two years ago: "It is hardly too much to say that it is difficult to see how a better book could be prepared for this purpose than the one before us." After the practical demonstration of two years' use of the book with his classes, his opinion is unchanged, and the additions in the present edition increase the value of the book. JAS. LEWIS HOWE.

INORGANIC CHEMISTRY ACCORDING TO THE PERIODIC LAW. By F. P. VENABLE AND JAS. LEWIS HOWE. Easton, Pa.: The Chemical Publishing Co. 1898. v+266 pp. 12mo. Price, $1.50.

Professor Venable's studies on the development of the Periodic Law have made so firm an impress on his mind that he has prepared a text-book for beginners in inorganic chemistry which takes the Periodic System as a guiding principle. The professor in the University of North Carolina has associated with him another experienced teacher in the person of Professor Howe, of the Washington and Lee University, and the two have produced a very systematic and accurate work quite up to date. In the hands of enthusiastic teachers the book cannot fail to prove useful in classes, especially if oral explanations supplement the concise and dogmatic statements. Whether beginners in chemistry are competent to appreciate the beauties of the Periodic System before they have learned something of the nature of chemical bodies in general, can be best determined by using the volume; but in any case the study of the terse introduction can be repeated after having read the first fifty or sixty pages. As the distinctive feature of this text-book is the order in which the elements and their compounds are treated, this review will endeavor to do it justice. After giving the history, methods of preparation, and the salient properties of hydrogen, as "the standard element," the elements of the negative subseries of Group VII of Mendeléeff's table are considered; this subseries includes fluorine, chlorine, bromine, and iodine.

Then follow the elements of the negative subseries of Groups VI and V; of Group IV both the positive and the negative series are included; of Group III, chiefly rare elements, only boron and aluminum are discussed; of Groups II and I both series are included. Then Group VIII is taken up, embracing the iron metals and the platinum metals. Part III is devoted to the hydrogen compounds of the elements and under the caption "Hydrids of Group VI" the student first makes the acquaintance of water. Part IV is devoted to halides, and Part V to oxides and sulphides, in which the student is introduced to carbon dioxide, lime, soda, nitrogen oxides, and sulphur oxides, including the important body sulphuric acid. Near the close of the volume there is a summary of the laws of constant proportion, of interproportionality, and of multiple proportions. Part VI deals with binary compounds of Groups V, IV, and with alloys.

The groups of the Periodic System, it will be observed, are discussed in the reverse order in which they appear in Mendeléeff's table, and the positive subseries are not taken up until after the negative. This inversion has been found necessary, probably, to avoid placing before the students the metals (sodium and associates, magnesium and associates, etc.), before the learner has made the acquaintance of the important bodies in Groups I and II (chlorine, bromine, iodine, oxygen, and sulphur). The necessity of consistently treating the elements in the order assigned to them by the Periodic Law leads to some curious results; thus the student finds himself studying selenium and tellurium before he has learned the most simple facts about the atmosphere; and in the same way tungsten, uranium, vanadium, columbium, and tantalum are met with before water. The oxides being in a section by themselves, are separated from the metals of which they form important compounds; thus it happens that between the account of the metal calcium and that of lime there are no less than eighty-six pages, and between lime and limestone there are twenty pages additional. Again the process of smelting iron is explained in connection with the description of the metal, just 150 pages before the characteristics of the oxides of the metal are given.

More attention is given in this book to the comparatively rare elements than is usual; thus more space is given to titanium

and germanium than to all the oxides of iron, and the elements molybdenum, tungsten, and uranium, with their compounds, occupy more space than calcium and its compounds in the several sections where they appear.

The book is clearly printed and quite free from typographical errors. The spelling recommended by the American Association for the Advancement of Science has been adopted only in part. Professor Howe, one of the committee on spelling and pronunciation, does not seem to have persuaded his colleague to accept the only rational orthography "sulfur."

Students using this volume will certainly not be misled and will become impressed with the importance of the Periodic Law.

H. CARRINGTON BOLTON.

COMMERCIAL ORGANIC ANALYSIS. VOL. II, PART I. BY ALFRED H. ALLEN, F.I.C., F.C.S., with revisions and addenda by the AUTHOR and HENRY LEFFMANN, M.A., M.D., Third Edition. Philadelphia: P. Blakiston's Son and Co. 8vo. 387 pp. Price $3.50.

The second edition of Volume II of Mr. Allen's valuable work appeared in 1886 and revision at this time was badly needed owing to the rapid advances which had been made in organic analysis. On this account the revision is quite thorough, almost every page and paragraph having been changed to meet the modern requirements. It has also been deemed necessary to divide the volume into two parts to avoid an unwieldy bulk and we now have before us, Part I.

The author and reviser have been compelled to cooperate at such long range, and the demand for the book has been so pressing that Dr. Leffmann has seen fit to assume the responsibility for any statements that do not meet the approval of the author and for any errors which may have crept into the book.

The work is exceptionally well done in every respect and reflects great credit upon the author and the reviser.

This part of Vol. II treats of the fixed oils and fats, glycerine, nitroglycerine, dynamites and smokeless powders, wool fats, dégras, etc. It contains also a list of corrections of the few errors found in Vol. I. Part II, which is now in press, will treat of the hydrocarbons and their immediate derivatives.

The most important additions made to the subjects treated in the volume before us, are: The bromine thermal method, meth-

ods for determination of glycerol, acetyl number, tests for oxidation of oils, composition and official methods for the examination of dynamites and smokeless powders, dégras and cloth oils.

Mr. Allen has added to the work some valuable tables giving the sources, specific gravities, solidifying-points, saponification-equivalents, iodine absorption, general characteristics and chief applications of the principal fats, oils, and waxes of commercial or scientific interest. WM. L. DUDLEY.

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Dietary Studies in Chicago in 1895 and 1896. Conducted with the Co-operation of Jane Addams and Caroline L. Hunt. Reported by W. O. Atwater and A. P. Bryant. Bulletin No. 55. U. S. Department of Agriculture, Office of Experiment Stations. Washington: Government Printing Office. 1898. 76 pp.

Michael Faraday: His Life and Work. By Silvanus P. Thompson, D.Sc., F.R.S. New York: The Macmillan Co. 1898. pp. ix + 308. Price, $1.25.

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Bulletins of the United States Geological Survey: No. 150.—The Educational Series of Rock Specimens Collected and Distributed by the United States Geological Survey. By J. S. Diller. 1898. 400 pp., 18 figures and 47 plates. No. 151.—The Lower Cretaceous Gryphæas of the Texas Region. By R. T. Hill and T. W. Vaughan. 1898. 66 pp. and 35 plates. No. 152.—A Catalogue of the Cretaceous and Tertiary Plants of North America. By F. H. Knowlton. 1898. 247 pp. No. 153.—A Bibliographic Index of North American Carboniferous Invertebrates. By Stuart Waller. 1898. 653 pp. No. 154.—A Gazetteer of Kansas. By Henry Gannett. 1898. 246 pp., 6 plates, and map of Kansas. No. 155.—Earthquakes in California in 1896 and 1897. By Charles D. Perrine. 1898. 46 pp. No. 156.—Bibliography and Index of North American Geology, Paleontology, Petrology, and Mineralogy for 1897. By Fred. B. Weeks. 1898. 130 pp. Washington: Government Printing Office.

Lighting by Acetylene.—Generators, Burners, and Electric Furnaces. By William E. Gibbs, M.E. Second Edition, Revised and Enlarged. New York: D. Van Nostrand Co. 1899. ix + 161 pp. Price, $1.50.

Physical Chemistry for Beginners. By Dr. Ch. Van Deventer. With an Introduction by Prof. J. H. van 't Hoff. Authorized American Edition from the German Edition, translated by Bertram B. Boltwood. New York: John Wiley & Sons. 1899. x+156 pp. Price, $1.50.

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